Dyes and Pigments 80 (2009) 187–193

Contents lists available at ScienceDirect

Dyes and Pigments

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

Novel porphyrazines containing peripherally functionalized macrocyclic (N_2O_2, N_2S_2) units: Synthesis and characterization

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A R T I C L E I N F O

Article history:
Received 9 May 2008
Received in revised form 2 July 2008
Accepted 3 July 2008
Available online 15 July 2008

Keywords:
Porphyrazine
Tetraazaporphyrin
Maleonitrile
Macrocycles
Magnesium
Zinc

A B S T R A C T

Novel maleonitrile moieties were synthesized by cyclization of 2,3-bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile with 1,2-bis(2-iodoethoxy)-4-nitrobenzene or *o*-xylyenebis(1-chloro-3-thiapropane) under conditions of high dilution. A series of novel, free-base, magnesium and zinc porphyrazines bearing macrocyclic substituents in peripheral positions were prepared via Linstead macrocyclization reactions of different maleonitrile derivatives, 12-nitro-4,7-bis(pyridin-2-ylmethyl)-2,3,4,7,8,9-hexahydro-1,10,4,7-benzodioxa-diaza-cyclododecine-5,6-dicarbonitrile or 5,8-bis(pyridin-2-ylmethyl)-1,3,4,5,8,9,10,12-octa-hydro-2,11,5,8-benzodi-thiadiazacyclo-tetradecine-6,7-dicarbonitrile and the corresponding divalent metal salts. Pentanuclear copper(II) complexes were also prepared from the corresponding zinc(II) porphyrazine derivatives. The compounds were characterized by a combination of elemental analysis, FT-IR, UV–vis, ^{1}H NMR, ^{13}C NMR and MS spectral data.

1. Introduction

Porphyrins, phthalocyanines and related macrocycles, modified by the attachment of peripheral substituents, have found vast applications in diverse areas such as elaboration of Langmuir–Blodgett films [1–3], chemical sensors [4], nonlinear optical materials [5], biomedical agents for diagnosis and therapy [6,7] as well as sensitizers in dye-sensitized solar cell applications [8,9]. In contrast, tetraazaporphyrazine or porphyrazines, the analogues of porphyrins and phthalocyanines, have been less well explored due to the lack of efficient synthetic methods. It has already been shown that the incorporation of crown ethers into other tetrapyrrole derivatives, namely phthalocyanines and porphyrins, results in products attractive as potential sensors for metal ions and as building blocks in supramolecular assemblies [10,11]. In contrast to fused phthalocyanine–crown ether systems, metal ion coordination by the crown ether units in $[(N_2,O_4\ \mathrm{crown})]_4$pz has profound effects on UV–vis spectra and other properties, since the key crown nitrogen residues are in direct electronic contact with the macrocyclic central chromophore [12]. In addition, the attachment of oxacrown [13], azacrown or polyaza–polythia macrocycles to porphyrazine has received considerable attention since they allow for cation selectivity and complex stability to be enhanced through changing the numbers and types of macrocycle donors as well as the solubility of porphyrazines [14–18]. Lastly, being isoelectronic in terms of π electrons with the PcH_2 skeleton, these types of polynucleating macrocyclic compounds are promising new materials with potential applications in different fields such as electron transfer [19], magnetic interactions [20], optical phenomena [21], excited-state reactivity [22], mixed valency [23], and ionophoric activity [24].

Our previous papers have described a series of phthalocyanines with various functional groups. These phthalocyanines have *N*-, *O*- and *S*-containing functionalities such as diazadioxa [25], cryptand [26,27], crown ether fused diloop [28], diazadithia macrocyclic with *tert*-butyl [29], and tetrathiamonoaza macrocyclic [30]. The immediate consequences of these peripheral substituents are enhanced solubility in common organic solvents and additional donor sites for alkali or transition metal ions.

In this paper, the synthesis and characterization of novel metal-free and metalloporphyrazines containing macrocyclic units have been described.

2. Experimental

All reactions were conducted under an atmosphere of argon and nitrogen using Schlenk techniques. 2,3-Bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile (**1**) [12], 1,2-bis(2-iodoethoxy)-4-

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doi:10.1016/j.dyepig.2008.07.002

nitrobenzene (**2**) [31] and o-xylylenebis(1-chloro-3-thiapropane) (**3**) [32] were prepared according to the literature procedures. All other reagents and solvents were of reagent grade quality obtained from commercial suppliers and were dried before use as described in the literature [33]. Column chromatography was carried out on silica gel (70–230 mesh) with the indicated eluents given in parentheses.

Melting points were determined by an electrothermal apparatus and were uncorrected. ^{1}H NMR, ^{13}C NMR and IR spectra were recorded on a Varian XL-200 spectrometer and on a Perkin–Elmer Spectrum One spectrometer with the samples in KBr pellets, respectively. Optical spectra in the UV–vis region were recorded with a model Shimadzu 1601 UV–vis spectrometer using a 1 cm pathlength cuvette at room temperature. Mass spectra were measured on Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. The elemental analysis and metal contents of the compounds were determined on a CHNS-932 LECO instrument and on a Unicam 929 AA spectrophotometer, respectively.

2.1. *12-Nitro-4,7-bis(pyridin-2-ylmethyl)-2,3,4,7,8,9-hexahydro-1,10,4,7-benzodioxadiaza-cyclododecine-5,6-dicarbonitrile (**4**)*

A 500 mL three-necked round-bottomed flask fitted with a condenser was charged with 300 mL of dry DMF and finely ground anhydrous Cs_2CO_3 (4.07 g, 12.5 mmol) and then evacuated, refilled three times with nitrogen, and connected to a vacuum line. Under nitrogen gas, the mixture was stirred at 50 °C for 15 min. Compound **1** (1.45 g, 5.0 mmol) and compound **2** (2.32 g, 5.0 mmol) in 30 mL of dry DMF were added dropwise over 8 h. After the addition was complete, the reaction mixture was heated for 36 h under nitrogen atmosphere. The reaction was monitored by a thin layer chromatography ($CHCl_3$–MeOH, 8.5:1.5). At the end of this period, the reaction mixture was allowed to cool to room temperature and stirred under nitrogen atmosphere for 24 h and then evaporated to dryness under reduced pressure. H_2O (100 mL) was added to the crude product and stirred for 30 min. Afterwards, $CHCl_3$ (50 mL) was added and stirred at room temperature for 15 min and extracted with 6 × 75 mL of $CHCl_3$. The organic phase was separated and dried over $MgSO_4$ and filtered off. The brown colored solution was evaporated to give the semi-solid product and the product was purified by column chromatography (silica gel, eluent $CHCl_3$–MeOH, 8.5:1.5 v/v). The brown solid was dissolved in 10 mL of ethyl acetate and kept inside the refrigerator at −18 °C for overnight. The precipitated brown solid product was collected via vacuum filtration and dried in vacuo to yield compound **4**. Yield: 1.05 g (42%); m.p. = 125–127 °C. $C_{26}H_{23}N_7O_4$ (497.51): calcd: C, 62.77; H, 4.66; N, 19.71%; found: C, 63.05; H, 4.34; N, 19.49%. IR (KBr): ν_{max} (cm^{-1}) = 3065 (CH aromatic), 2932–2870 (CH_2 aliphatic), 2214 (C≡N), 1589 (NO_2), 1512, 1340 (NO_2), 1275, 1235 (Ar–O), 1146, 1096, 747, 621. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 8.50$–8.46 (m, 2H), 7.92–7.80 (m, 6H), 7.35–7.14 (m, 3H), 4.50 (s, 4H, NC*H*$_2$-py), 4.11 (t, 4H, C*H*$_2$OAr), 3.48 (t, 4H, NC*H*$_2$CH$_2$O). ^{13}C NMR (ppm, $CDCl_3$): $\delta = 157.2$, 152.2, 148.9, 146.8, 140.6, 135.7, 124.0, 122.4, 117.8, 116.5, 114.9, 112.6, 108.2, 71.9, 54.7, 50.8. MS (ES$^+$) *m*/*z*: 498.7 $[M+H]^+$, 404.3 $[M-PyCH_2+H]^+$, 94.2 $[PyCH_2+2H]^+$.

2.2. *5,8-Bis(pyridin-2-ylmethyl)-1,3,4,5,8,9,10,12-octahydro-2,11,5,8-benzodithiadiazacyclo-tetradecine-6,7-dicarbonitrile (**5**)*

A 500 mL three-necked round-bottomed flask fitted with a condenser was charged with 300 mL of dry DMF, finely ground anhydrous Cs_2CO_3 (10.75 g, 32.95 mmol) and anhydrous NaI (0.1 g, 0.67 mmol), and then evacuated, refilled three times with nitrogen, and connected to a vacuum line. The mixture was stirred at 60 °C for 20 min under a N_2 gas. A mixture of compound **1** (3.83 g, 13.20 mmol) and compound **3** (3.90 g, 13.20 mmol) in DMF (40 mL) was added to the reaction mixture dropwise over 8 h. Afterwards, the reaction mixture was stirred at 60 °C for 62 h. The reaction was monitored by a thin layer chromatography (EtOAc:MeOH, 9.5:0.5). At the end of this period, the mixture was allowed to cool to room temperature and then evaporated to dryness under reduced pressure. A mixture of $CHCl_3$:H_2O (1:1 v/v, 200 mL) was added to brown colored semi-solid product and stirred for 2 h. The organic phase was separated and the aqueous phase was extracted with 5 × 100 mL of $CHCl_3$ and combined organic layers were dried over $MgSO_4$ and filtered off. The solvent was evaporated. The obtained crude product was dissolved in minimum amount of EtOH, and Et_2O (3 mL) was added to maintain precipitation and then kept inside the refrigerator at −18 °C for overnight. The resulting brown solid product was collected via vacuum filtration and dried in vacuo to yield compound **5**. Yield: 1.82 g (27%); m.p. = 158–161 °C. $C_{28}H_{28}N_6S_2$ (512.69): calcd: C, 65.60; H, 5.50; N, 16.39; S, 12.51%; found: C, 66.01; H, 5.18; N, 16.64; S, 12.78%. IR (KBr): ν_{max} (cm^{-1}) = 3055 (CH aromatic), 2919–2850 (CH_2 aliphatic), 2216 (C≡N), 1590, 1569, 1467–1434, 1286, 1151, 1048, 995, 752, 667, 625. ^{1}H NMR (ppm, DMSO-*d*$_6$): $\delta = 8.60$–8.56 (m, 2H), 8.02–7.90 (m, 4H), 7.35–7.29 (m, 2H), 7.18–7.04 (m, 4H), 4.41 (s, 4H, NC*H*$_2$-py), 3.92 (s, 4H, SC*H*$_2$Ar), 3.29 (t, 4H, NC*H*$_2$CH$_2$S), 2.75 (t, 4H, NCH$_2$C*H*$_2$S). ^{13}C NMR (ppm, DMSO-*d*$_6$): $\delta = 156.2$, 149.2, 137.2, 135.8, 130.4, 127.6, 123.9, 121.7, 115.6, 113.5, 53.0, 50.2, 35.8, 33.4. MS (ES$^+$) *m*/*z*: 513.9 $[M+H]^+$, 421.8 $[M-PyCH_2+H]^+$, 94.2 $[PyCH_2+2H]^+$.

2.3. *Porphyrazinato magnesium(II) (**6**)*

A mixture of Mg turnings (24 mg, 1 mmol) in dry 1-BuOH (30 mL) was heated at reflux for 24 h under an Ar gas using a few crystals of iodine to initiate the reaction. The dinitrile derivative **4** (1.0 g, 2 mmol) was added to the resulting magnesium butoxide suspension and the suspension was refluxed with stirring for a further 48 h. Afterwards, the mixture was filtered while hot and the residue was washed with $CHCl_3$ (75 mL). The combined organic solutions were evaporated under vacuum. The resulting solid was chromatographed ($CHCl_3$–MeOH:NH_4OH, 98:1.5:0.5) to afford the Mg-porphyrazine **6** as a dark blue solid. Yield: 233 mg (23%); m.p. > 300 °C. $C_{104}H_{92}MgN_{28}O_{16}$ (2014.36): calcd: C, 62.01; H, 4.60; Mg, 1.21; N, 19.47%; found: C, 61.85; H, 4.87; Mg, 1.49; N, 19.05%. IR (KBr): ν_{max} (cm^{-1}) = 3060 (CH aromatic), 2920–2856 (CH_2 aliphatic), 1625 (C=N), 1587 (NO_2), 1530, 1343 (NO_2), 1270, 1230 (Ar–O), 1120, 1080, 760, 630. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 8.87$–8.52 (m, 8H), 7.87–7.64 (m, 24H), 7.10–6.90 (m, 12H), 5.48 (s, br, 16H, NC*H*$_2$-py), 4.23–4.12 (m, br, 16H, C*H*$_2$OAr), 3.24–3.13 (m, br, 16H, NC*H*$_2$CH$_2$O). ^{13}C NMR (ppm, DMSO-*d*$_6$): $\delta = 161.4$, 152.4, 151.8, 148.5, 146.1, 141.3, 137.3, 136.4, 123.2, 122.1, 118.4, 112.5, 108.2, 71.6, 57.8, 51.6. UV–vis ($CHCl_3$) λ_{max} (log ε) = 351 (4.79), 576 (4.18), 666 (4.52). MS (ES$^+$) *m*/*z*: 2015.5 $[M+H]^+$.

2.4. *Porphyrazinato magnesium(II) (**7**)*

A suspension of magnesium butoxide was prepared by heating a mixture of Mg (48 mg, 2 mmol) in 1-butanol (60 mL) at reflux for 24 h under an Ar gas and with the addition of a small chip of I_2 to initiate the reaction. Dinitrile derivative **5** (2.05 g, 4 mmol) was added to this solution (maintained at reflux). The solution was kept at reflux for a period of 36 h after which it was cooled to 80 °C and the solvent evaporated by vacuum distillation. The solid residue was dissolved in $CHCl_3$ (400 mL) and filtered through a pad of Celite. The filtrate was rotary evaporated and chromatographed ($CHCl_3$–MeOH:NH_4OH, 87:2.5:0.5) to yield the Mg-porphyrazine **7** as a dark blue solid. Yield: 353 mg (17%); m.p. > 300 °C. $C_{112}H_{112}MgN_{24}S_8$ (2075.07): calcd: C, 64.83; H, 5.44; Mg, 1.17; N, 16.20; S, 12.36%; found: C, 65.23; H, 5.64; Mg, 1.06; N, 15.92; S, 12.13%. IR (KBr): ν_{max} (cm^{-1}) = 3060 (CH aromatic), 2930–2855

(CH_2 aliphatic), 1630 (C=N), 1587, 1565, 1460–1430, 1275, 1164, 1070, 960, 754, 660, 620. ^1H NMR (ppm, DMSO-d_6): $\delta = 8.79–8.60$ (m, 8H), 8.13–7.82 (m, 16H), 7.40–7.32 (m, 8H), 7.10–6.94 (m, 16H), 5.20 (s, br, 16H, NCH_2-py), 3.95 (s, br, 16H, SCH_2Ar), 3.32–3.24 (m, 16H, NCH_2CH_2S), 2.70–2.66 (m, br, 16H, NCH_2CH_2S). ^{13}C NMR (ppm, DMSO-d_6): $\delta = 160.3$, 152.5, 148.3, 137.2, 136.7, 135.6, 130.2, 127.7, 123.5, 121.6, 58.2, 52.3, 35.4, 33.1. UV–vis ($CHCl_3$) λ_{max} (log ε) = 365 (4.96), 579 (4.28), 662 (4.83). MS (ES^+) *m/z*: 2076.2 $[M+H]^+$.

2.5. Metal-free porphyrazine (**8**)

Mg-porphyrazine **6** (0.20 g, 0.1 mmol) was dissolved in CF_3CO_2H (2.5 mL) and stirred at room temperature in the dark for 2 h. The solution was poured over ice (100 g) and then neutralized with 2 M NaOH. The mixture was kept in the refrigerator overnight to complete the precipitation. The precipitated solid was filtered, washed extensively with distilled water and dried in vacuo. Chromatography ($CHCl_3$–MeOH, 80:20) gave porphyrazine **8** as a dark green solid. Yield: 148 mg (75%); m.p. > 300 °C. $C_{104}H_{94}N_{28}O_{16}$ (1992.07): calcd: C, 62.71; H, 4.76; N, 19.69%; found: C, 62.97; H, 4.42; N, 19.91%. IR (KBr): ν_{max} (cm^{-1}) = 3265 (N–H), 3063 (CH aromatic), 2960–2865 (CH_2 aliphatic), 1620 (C=N), 1590 (NO_2), 1520, 1345 (NO_2), 1264, 1235 (Ar–O), 1125, 1070, 1030, 765, 640. ^1H NMR (ppm, $CDCl_3$): $\delta = 8.69–8.47$ (m, 8H), 7.90–7.60 (m, 24H), 7.15–6.97 (m, 12H), 5.29 (s, br, 16H, NCH_2-py), 4.30–4.18 (m, br, 16H, CH_2OAr), 3.31–3.26 (m, br, 16H, NCH_2CH_2O), −0.90 (s, br, 2H). ^{13}C NMR (ppm, DMSO-d_6): $\delta = 162.2$, 151.9, 150.6, 149.1, 145.9, 141.4, 137.8, 135.9, 124.3, 122.4, 119.1, 111.9, 107.9, 70.9, 58.6, 51.7. UV–vis ($CHCl_3$) λ_{max} (log ε) = 348 (4.94), 578 (4.30), 665 (4.60), 724 (4.70). MS (ES^+) *m/z*: 1993.2 $[M+H]^+$.

2.6. Metal-free porphyrazine (**9**)

Mg-porphyrazine **7** (0.21 g, 0.1 mmol) was treated with CF_3CO_2H (4 mL) and mixed at room temperature in the dark for 3 h and poured over crushed ice (100 g). The residue was rinsed with H_2O (100 mL) and the washings combined with the ice solution. The pH of the solution was raised to 12 by the addition of concentrated aqueous NH_3 and the precipitated solid collected by filtration. The solid was washed copiously with H_2O and MeOH until the washings were clear. The pure product **9** was obtained as a dark blue solid following chromatography ($CHCl_3$–MeOH, 95:5). Yield: 198 mg (87%); m.p. > 300 °C. $C_{112}H_{114}N_{24}S_8$ (2052.78): calcd: C, 65.53; H, 5.60; N, 16.38; S, 12.49%; found: C, 65.82; H, 5.39; N, 16.65; S, 12.93%. IR (KBr): ν_{max} (cm^{-1}) = 3280 (N–H), 3062 (CH aromatic), 2960–2825 (CH_2 aliphatic), 1624 (C=N), 1585, 1556, 1462–1425, 1272, 1145, 1032, 974, 748, 672, 635. ^1H NMR (ppm, DMSO-d_6): $\delta = 8.90–8.63$ (m, 8H), 8.20–7.85 (m, 16H), 7.38–7.26 (m, 8H), 7.13–6.87 (m, 16H), 5.32 (s, br, 16H, NCH_2-py), 3.93 (s, br, 16H, SCH_2Ar), 3.30–3.21 (m, 16H, NCH_2CH_2S), 2.76–2.69 (m, br, 16H, NCH_2CH_2S). ^{13}C NMR (ppm, DMSO-d_6): $\delta = 160.6$, 151.8, 148.1, 137.4, 136.3, 135.9, 130.5, 127.3, 122.8, 121.3, 59.7, 52.3, 35.6, 33.4. UV–vis ($CHCl_3$) λ_{max} (log ε) = 345 (4.91), 575 (4.20), 670 (4.47), 712 (4.59). MS (ES^+) *m/z*: 2053.9 $[M+H]^+$.

2.7. Porphyrazinato zinc(II) (**10**)

A 50 mL three-necked round-bottomed flask fitted with a condenser was charged with porphyrazine **8** (100 mg, 0.05 mmol), $Zn(OAc)_2$ (92 mg, 0.5 mmol) in a mixture of DMF (4 mL) and PhCl (8 mL) and then evacuated, refilled three times with nitrogen, and connected to a vacuum line. The mixture was heated to 100 °C under a N_2 gas and stirred for 16 h. The solvent was then removed by vacuum distillation, and the solid residue was washed with 1% HCl/MeOH and filtered. The resultant solid was washed with H_2O, MeOH and Et_2O. Product **10** was isolated as a dark blue powder following chromatography (3% MeOH/$CHCl_3$). Yield: 87 mg (84%); m.p. > 300 °C. $C_{104}H_{92}N_{28}O_{16}Zn$ (2055.43): calcd: C, 60.77; H, 4.51; N, 19.08; Zn, 3.18%; found: C, 61.14; H, 4.23; N, 18.76; Zn, 3.47%. IR (KBr): ν_{max} (cm^{-1}) = 3062 (CH aromatic), 2929–2852 (CH_2 aliphatic), 1632 (C=N), 1586 (NO_2), 1538, 1347 (NO_2), 1268, 1242 (Ar–O), 1124, 1069, 763, 634. ^1H NMR (ppm, DMSO-d_6): $\delta = 8.9–8.60$ (m, 8H), 7.83–7.67 (m, 24H), 7.21–6.98 (m, 12H), 5.35 (s, br, 16H, NCH_2-py), 4.27–4.15 (m, br, 16H, CH_2OAr), 3.31–3.17 (m, br, 16H, NCH_2CH_2O). UV–vis ($CHCl_3$) λ_{max} (log ε) = 354 (4.98), 583 (4.04), 658 (4.76). MS (ES^+) *m/z*: 2056.7 $[M+H]^+$.

2.8. Porphyrazinato zinc(II) (**11**)

A 50 mL three-necked round-bottomed flask fitted with a condenser was charged with porphyrazine **9** (102.63 mg, 0.05 mmol), $Zn(OAc)_2$ (92 mg, 0.5 mmol) in a mixture of DMF (5 mL) and PhCl (15 mL) and then evacuated, refilled three times with nitrogen, and connected to a vacuum line. The mixture was heated to 100 °C under a N_2 gas and stirred for 18 h. Afterwards, the mixture was filtered while hot through Celite, and the solvent was evaporated. The solid residue was washed with 1% HCl/MeOH and filtered. The resultant solid was washed with H_2O, MeOH and Et_2O and chromatographed ($CHCl_3$) to yield porphyrazinato zinc(II) **11** as a dark blue solid. Yield: 97 mg (92%); m.p. > 300 °C. $C_{112}H_{112}N_{24}S_8Zn$ (2116.14): calcd: C, 63.57; H, 5.33; N, 15.38; S, 12.12; Zn, 3.09%; found: C, 63.29; H, 5.61; N, 15.57; S, 12.48; Zn, 3.46%. IR (KBr): ν_{max} (cm^{-1}) = 3064 (CH aromatic), 2965–2840 (CH_2 aliphatic), 1637 (C=N), 1583, 1562, 1472–1430, 1263, 1142, 1044, 964, 752, 665, 627. ^1H NMR (ppm, DMSO-d_6): $\delta = 8.85–8.57$ (m, 8H), 8.12–7.78 (m, 16H), 7.30–7.19 (m, 8H), 7.06–6.92 (m, 16H), 5.28 (s, br, 16H, NCH_2-py), 3.90 (s, br, 16H, SCH_2Ar), 3.36–3.27 (m, 16H, NCH_2CH_2S), 2.79–2.64 (m, br, 16H, NCH_2CH_2S). UV–vis ($CHCl_3$) λ_{max} (log ε) = 350 (4.99), 580 (3.78), 668 (4.81). MS (ES^+) *m/z*: 2117.3 $[M+H]^+$.

2.9. Copper(II) complexes of **10** and **11** (**12**, **13**)

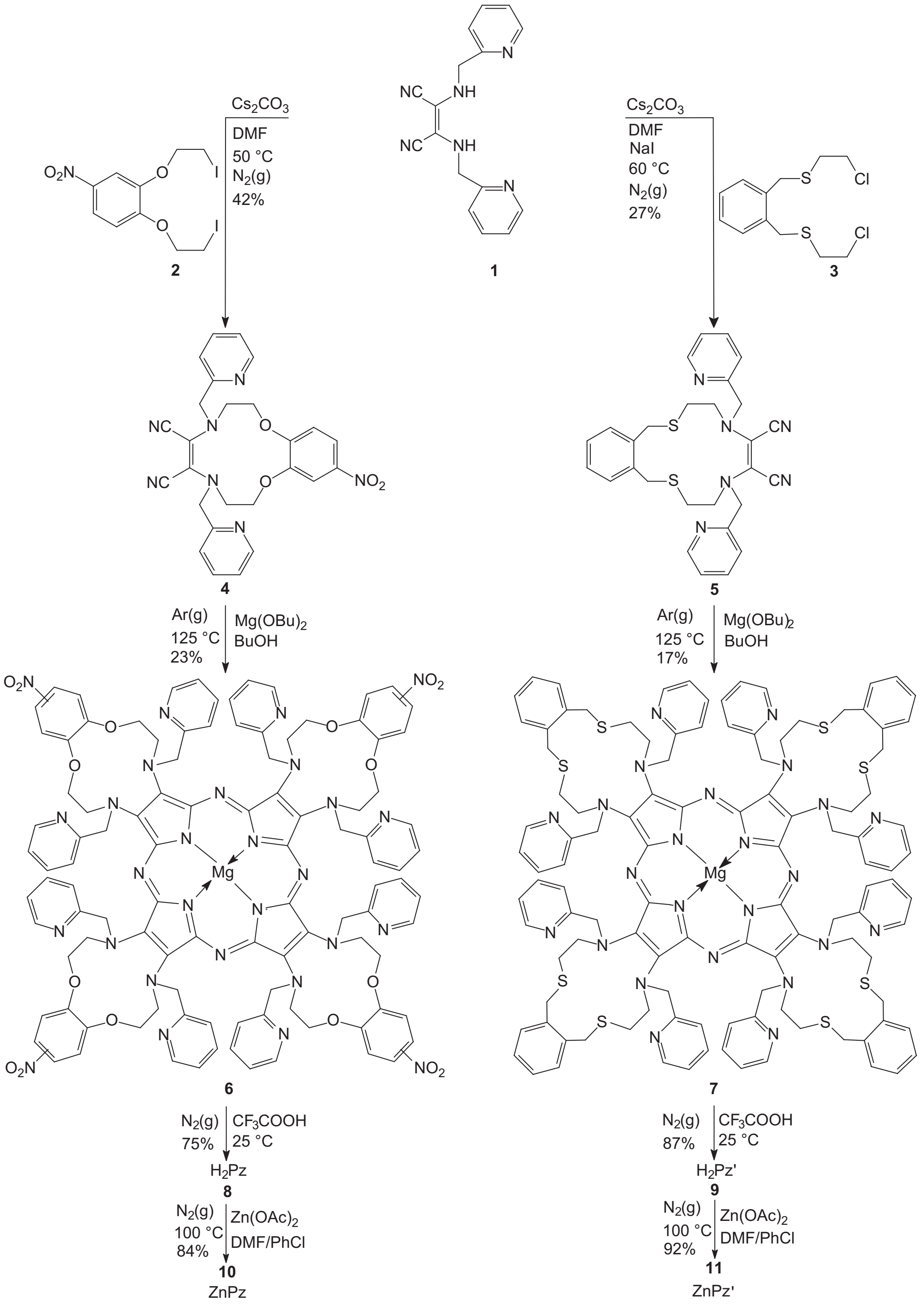
Zinc(II) porphyrazine derivative **10** (51.4 mg, 0.025 mmol) or **11** (53.0 mg, 0.025 mmol) was dissolved in tetrahydrofuran/water (5.1:0.1) in a 50-mL three-necked round-bottomed flask. Copper(II) perchlorate hexahydrate (75.6 mg, 0.2 mmol) was added to the same solvent mixture (5.1:0.1). The mixture was heated at reflux for 3 h, and a bluish-green product was formed. The product was separated by centrifugation and washed several times successively with hot water, hot ethanol, and then diethyl ether. The deep blue products were then dried with P_2O_5 in vacuo.

For **12**, yield: 57.80 mg (74%); m.p. > 300 °C. $C_{104}H_{92}Cl_8Cu_4N_{28}O_{48}Zn$ (3105.22): calcd: C, 40.23; H, 2.99; Cu, 8.19; N, 12.63; Zn, 2.11%; found: C, 39.97; H, 3.18; Cu, 8.45; N, 12.43; Zn, 1.93%. IR (KBr): ν_{max} (cm^{-1}) = 3057 (CH aromatic), 2960–2875 (CH_2 aliphatic), 1635 (C=N), 1589 (NO_2), 1554, 1345 (NO_2), 1270, 1245 (Ar–O), 1145–1042 (ClO_4^{-1}), 967, 769, 635 (ClO_4^{-1}), 620. UV–vis (pyridine) λ_{max} (log ε) = 335 (4.88), 657 (4.78). MS (ES^+) *m/z*: 3106.4 $[M+H]^+$.

For **13**, yield: 64.97 mg (82%); m.p. > 300 °C. $C_{112}H_{112}Cl_8Cu_4N_{28}O_{32}S_8Zn$ (3165.93): calcd: C, 42.49; H, 3.57; Cu, 8.03; N, 10.62; S, 8.10; Zn, 2.07%; found: C, 42.67; H, 3.30; Cu, 8.26; N, 10.85; S, 8.39; Zn, 2.28%. IR (KBr): ν_{max} (cm^{-1}) = 3060 (CH aromatic), 2985–2820 (CH_2 aliphatic), 1635 (C=N), 1580, 1559, 1480–1439, 1265, 1150–1040 (ClO_4^{-1}), 960, 756, 642 (ClO_4^{-1}), 626. UV–vis ($CHCl_3$) λ_{max} (log ε) = 317 (4.89), 654 (4.73). MS (ES^+) *m/z*: 3166.9 $[M+H]^+$.

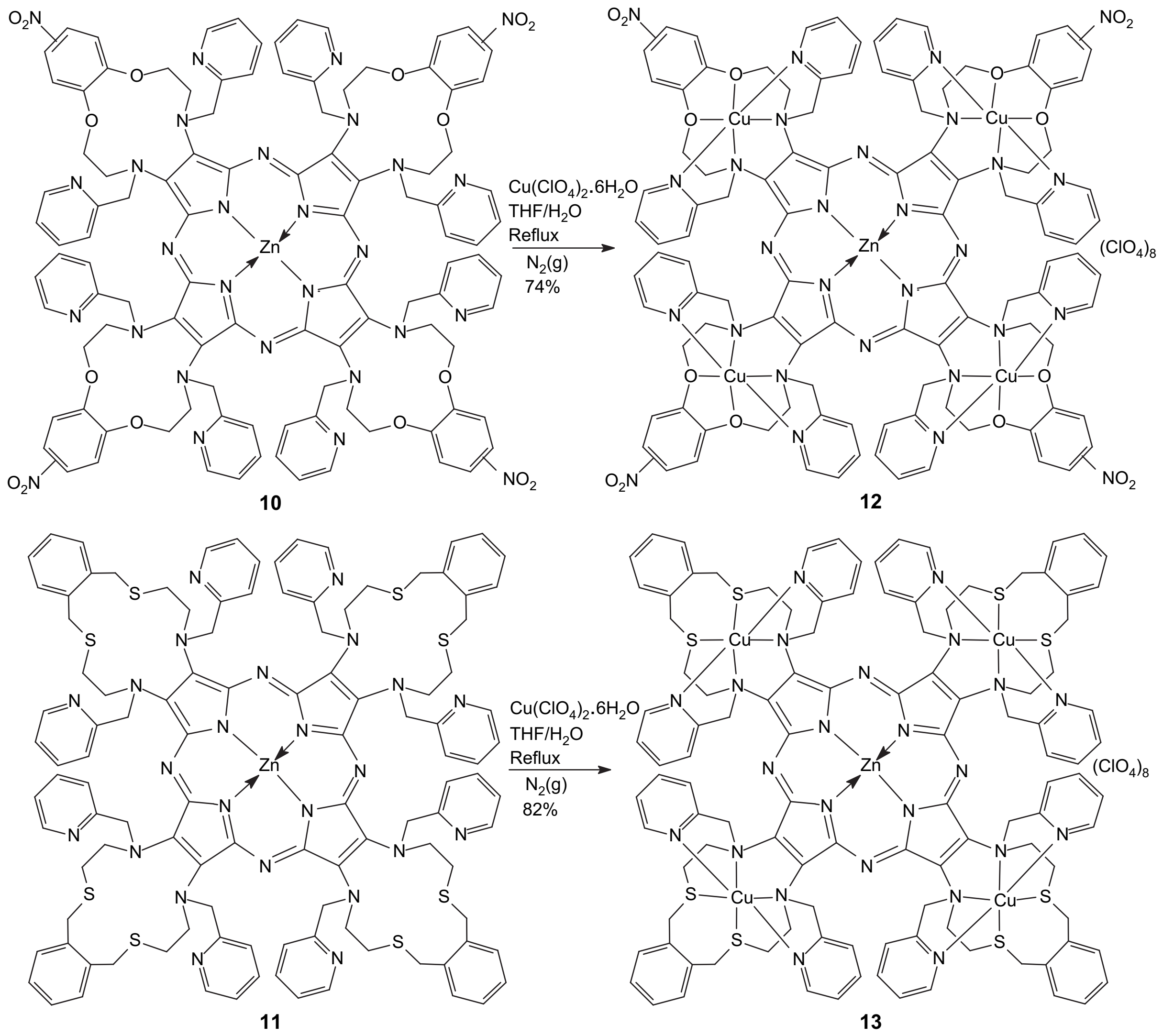
3. Results and discussion

The synthetic routes related to compounds **4**–**11** are summarized in Scheme 1 and for **12** and **13** in Scheme 2. In this work, we reported the synthesis and structural properties of a series of novel



Scheme 1. Synthesis of metal-free and metalloporphyrazines.

metal-free and metalloporphyrazine derivatives. Compound **4** was obtained by an addition reaction of compound **1** (2,3-Bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile) [12] and compound **2** (1,2-bis(2-iodoethoxy)-4-nitrobenzene) [31] in the presence of anhydrous Cs_2CO_3 and dry DMF at 50 °C for 36 h under nitrogen gas in 42% yield. Compound **4** was characterized by its spectroscopic and analytical data. The IR spectrum of **4** was verified with the disappearance of vibrations relating to N–H groups of compound **1** and the presence of aromatic ring, NO_2 group and C≡N stretching vibrations at 3065, 1589–1340 and 2214 cm^{-1}, respectively. In the ^1H NMR spectrum of **4**, the multiplet signals at 8.50–8.46, 7.92–7.80 and 7.35–7.14 ppm correspond to aromatic protons in the body of compound **4**. Further, some other characteristic signals were observed for (NCH_2-py), (CH_2OAr) and (NCH_2CH_2O) protons at $\delta = 4.50$, 4.11, and 3.48 ppm, respectively. Proton-decoupled ^{13}C NMR spectral data were in good agreement with the proposed structure. The LC/ES mass spectrum of **4**, which displays a peak corresponding to $[M+H]^+$ at $m/z = 498.7$ and also other



Scheme 2. Synthesis of pentanuclear metalloporphyrazines (**12**, **13**).

fragmentations at $m/z = 404.3$ $[M - PyCH_2 + H]^+$ and 94.2 $[PyCH_2 + 2H]^+$, confirms the proposed structure.

Compound **5** was obtained from the reaction of compound **1** (2,3-Bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile) [12] and compound **3** (*o*-xylyenebis(1-chloro-3-thiapropane)) [32] in 27% yield after overall treatments. The disappearance of the signals of N–H groups and the appearance of C≡N stretching vibrations at 2216 cm^{-1} in the IR spectrum supported the formation of dicyano derivative **5**. ^1H NMR spectrum of **5** exhibited aromatic proton signals at $\delta = 8.60–8.56$, 8.02–7.90, 7.35–7.29, 7.18–7.04 ppm, respectively. Some other characteristic signals were observed for (NCH_2-py), (SCH_2Ar), (NCH_2CH_2S) and (NCH_2CH_2S) protons at $\delta = 4.41$, 3.92, 3.29 and 2.75 ppm, respectively, in the ^1H NMR spectrum of **5**. Proton-decoupled ^{13}C NMR spectral data were in good agreement with the proposed structure. In the ES mass spectra of compound **5**, a peak corresponding to $[M + H]^+$ at $m/z = 513.9$ and also other fragmentations at $m/z = 421.8$ $[M - PyCH_2 + H]^+$ and 94.2 $[PyCH_2 + 2H]^+$, were in a good accord with the suggested structure. Attempted formation of macrocyclic compound **5** using the ditosylate corresponding to **3** with potassium *tert*-butoxide, sodium or potassium hydrides, or sodium or potassium carbonates as base or from the reaction of **3** using sodium or potassium hydrides as base or at higher temperatures gave significantly reduced yields of macrocyclic compound **5** (5–17%). Similar to the synthesis of dithiadiaza macrocyclic **5**, slow addition of a solution of diamine **1** and dichloride **3** in DMF to a suspension of cesium carbonate, NaI in DMF afforded the macrocyclic compound **5** in 27% yield (Scheme 1).

Porphyrazinato magnesium(II) **6** and **7** were obtained as dark blue solids from Linstead macrocyclization [34] of compounds **4** and **5**, Mg turnings and dry 1-BuOH under Argon gas using a small chip of I_2 in 23% and 17% yields, respectively, after purification by chromatography. According to the IR spectrum of **6** and **7**, the signals for C≡N groups at 2214 and 2216 cm^{-1}, respectively, for compounds **4** and **5** disappeared and new peaks arose at 1625 and 1630 cm^{-1} that are dedicated to C=N bonds in porphyrazine core of **6** and **7**, respectively. Except for some little changes, other vibrations in IR spectrum were very similar to compounds **4** and **5**. The peaks relating to C≡N groups in the ^{13}C NMR spectrum of **4** and **5** vanished in case of Mg-porphyrazines **6** and **7**. Other ^1H NMR and ^{13}C NMR spectrum peaks were similar to those of the precursor compounds **4** and **5**. In addition to the results of elemental analysis, the mass spectra were determined and the peaks referring to $[M + H]^+$ at $m/z = 2015.5$ and 2076.2 were found by the ES^+ technique for porphyrazinato magnesium(II) **6** and **7** respectively.

Metal-free porphyrazines **8** and **9** were obtained in 75% and 87% yields as dark green and dark blue solids by the demetallization of porphyrazinato magnesium(II) **6** and **7** after chromatographic procedures. The formation of N–H bonds in porphyrazine core of compounds **8** and **9** was observed at 3265 and 3280 cm^{-1}, respectively, in the IR spectrum of **8** and **9**. ^1H NMR spectra of compound **8** exhibited a signal at $\delta = -0.90$ ppm, which indicates the inner core protons of N–H groups of porphyrazines **8**. A common feature of the ^1H NMR spectrum of **9** is the broad absorption caused probably by the aggregation of H_2Pz', which is frequently encountered at the concentration used for NMR measurements [25,35]. The inner core protons of this compound could also not be observed because of strong aggregation of the molecule [25,36,37]. ^1H NMR and ^{13}C NMR spectra of **8** and **9** were very similar to those of the precursor compounds **6** and **7**. Mass spectra (ES positive) at $m/z = 1993.2$ and 2053.9 $[M+H]^+$ proved the structures of **8** and **9** as well as elemental analysis.

Porphyrazinato zinc(II) **10** and **11** were prepared from compounds **8** and **9**, $Zn(OAc)_2$ and a mixture of DMF and PhCl under a N_2 gas atmosphere in 84% and 92% yields as a dark blue powder and a dark blue solid, respectively. In the IR spectra of compounds **10** and **11**, N–H bonds in porphyrazine core of compounds **8** and **9** at 3265 and 3280 cm^{-1} vanished. Other IR vibrations of **10** and **11** are so familiar with compounds **8** and **9** except for some little changes. The signal of N–H groups that was observed due to the inner core of precursor metal-free porphyrazine derivative **8** disappeared in case of compound **10**. Other ^1H NMR spectra of **10** and **11** were very similar to those of the precursor compounds **8** and **9**. In the ES positive mass spectral data of compounds **10** and **11**, the peaks corresponding to $[M+H]^+$ at $m/z = 2056.7$ and 2117.3 are in a good accord with recommended structures. The results of elemental analysis and the mass spectral data for the metalloporphyrazines **6**, **7**, **10** and **11** confirmed that the ratio of reactants was 1:1 (metal:ligand).

It is well known that cyclotetramerization of this type of substituted phthalonitrile **5** leads to the formation of four constructional isomers. It could be deduced from the broadening of absorption peaks of ^1H NMR, and TLC analysis that metal-free and metalloPcs (**6**, **8**, **10**, **12**) are a mixture of four isomers. To the best of our knowledge, there is no literature presently that reports the successful separation of these four isomers with ordinary column chromatography except for a paper [38]. According to that paper, only the two isomers (C_{4h}, C_{2v}) could be isolated by column chromatography, but the other two isomers (D_{2h}, C_s) could not be. Our attempts to separate these isomers by column chromatography were not successful. However, Hanack and coworkers separated all four isomers of different tetrasubstituted Pcs by HPLC [39,40].

Copper(II) complexes **12** and **13** were obtained as deep blue solids from zinc(II) porphyrazine derivatives **10** and **11** as described in experimental section with 74% and 82% yields, respectively. In the IR spectra of **12** and **13**, the vibrations corresponding to perchlorate peaks at 1145–1042 and 635 cm^{-1} for compound **12**, and 1150–1040 and 642 cm^{-1} for compound **13** confirmed the proposed structures. Elemental analyses and mass spectral data are in a good accord with **12** and **13**. NMR spectra of copper(II) complexes **12** and **13** could not be taken due to the paramagnetic nature of copper centers.

The electronic absorption spectra of the metalloporphyrazines **6**, **7**, **10** and **11** taken in $CHCl_3$ and **12**, **13** in pyridine at room temperature exhibit a strong absorption between 658 and 668 nm which is due to a $\pi \rightarrow \pi^*$ transition and is commonly referred to as Q band. A second intense and broad $\pi \rightarrow \pi^*$ transition in the range 300–365 nm which is called Soret or B band is also a characteristic of these tetrapyrrole derivatives (Fig. 1) [41–43]. In addition, heteroatom-substituted porphyrazines display intense coupling between the nonbonding, lone pair electrons and the macrocyclic π-system. The resultant $n \rightarrow \pi^*$ transitions (transitions attributed to the nonbonding peripheral nitrogen electron (n) to the π^* pz orbital) were visible in the electronic absorption spectra (∼570–580 nm) [44]. The strong coupling of the nonbonding electrons with the π-system also resulted in significant broadening due to vibrational fine structure. As expected, the metal-free derivatives **8** and **9** show a splitted Q band because of the change in symmetry from D_{4h} in metallo-species to D_{2h} in free-base ones (Fig. 2). UV–vis studies were also performed with copper(II) perchlorate hexahydrate (see Fig. 2) to investigate the metal-binding capabilities of porphyrazines **10** and **11**. In the UV–vis spectra of porphyrazines (**10**, **11**) containing peripheral nitrogen atoms, the disappearance of $n \rightarrow \pi^*$ absorbance and a sharpening of the Q band indicate metal coordination to the peripheral nitrogen atoms. Because the nitrogen n electrons are no longer available to the porphyrazine π-system, metal coordination to the peripheral nitrogen atoms ultimately results in a spectrum that resembles an unsubstituted porphyrazine or phthalocyanine [12,15,45]. Aggregation of symmetrical porphyrazine and phthalocyanines can be efficiently followed from band broadening to a blue shift of the Q bands. However, spectra recorded at 1×10^{-4} and 1×10^{-5} M solutions of porphyrazines **6**–**14** in chloroform or pyridine are

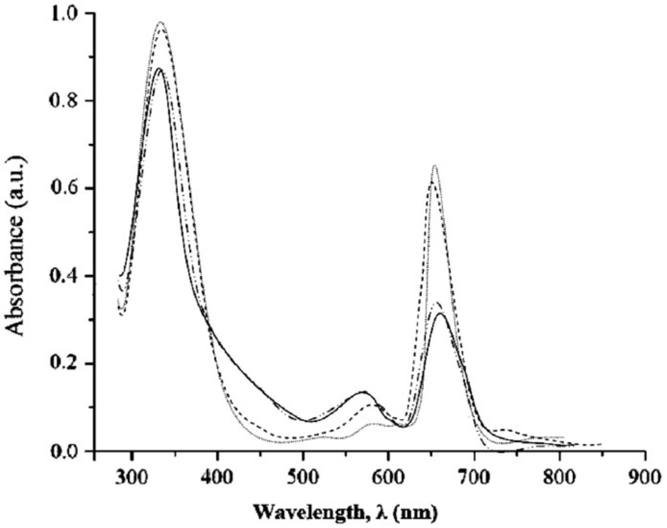


Fig. 1. Electronic spectra of **6** (—) (1.0 × 10^{-5} M), **7** (–··–) (1.0 × 10^{-5} M), **10** (- - -) (1.0 × 10^{-5} M) and **11** (...) (1.0 × 10^{-5} M) in $CHCl_3$.

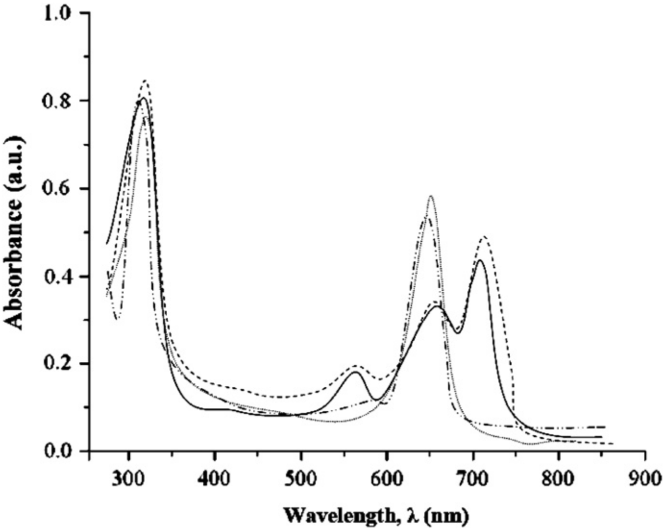


Fig. 2. Electronic spectra of **8** (- - -), **9** (—) in $CHCl_3$ (1.0 × 10^{-5} M), and **12** (...) and **13** (–··–) in pyridine (1.0 × 10^{-5} M).

identical in shape, implying that aggregation is not very effective in the present case. This might be attributed to the bulky nature of the peripheral substituents which prevents the interactions between porphyrazine cores at least in these concentrations. Similarly, negligible differences between the spectra obtained in different solvents (chloroform, dichloromethane and pyridine) can also be taken as a further confirmation of this proposal.

Acknowledgements

This study was supported by The Scientific and Technical Research Council of Turkey (TUBITAK), project number: TBAG-2453(104T065) (Ankara, Turkey) and the Research Fund of Karadeniz Technical University, project number: 2002.111.2.8 (Trabzon/Turkey).

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