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Synthesis and electrochemical properties of porphyrazines with annulated 1,4-dithiaheterocycles

Behice Şebnem Sesalan [a], Atıf Koca [b], Ahmet Gül [a,*]

[a] Department of Chemistry, Technical University of Istanbul, Maslak 34469, Istanbul, Turkey
[b] Chemical Engineering Department, Engineering Faculty, Marmara University, Kadıköy, Istanbul, Turkey

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Abstract

Porphyrazines (M = H, Mg, Zn or Cu) with 2,3-trimethyleneoxy-2,3-dihydro-1,4-dithiin or 2-ethoxy-2,3-dihydro-1,4-dithiin groups fused to each pyrrol unit have been synthesised starting with the corresponding unsaturated dicarbonitrile derivative. The elemental analysis and IR, ^{1}H NMR, UV–Vis and mass spectral data have been used to characterise the new compounds. Electrochemical investigations have shown that metal insertion into the porphyrazine core and substituents having high electron donating ability shift the ring centred reduction processes towards negative potentials.

Keywords: Porphyrazines; Phthalocyanines; Magnesium; Copper; Zinc; Electrochemistry

1. Introduction

Since the discovery of the phthalocyanine macrocycle at the beginning of the 20th Century, porphyrins and phthalocyanines have become the focus of intense research interest due to their somewhat peculiar properties for diverse applications [1]. Among these properties we might include planar molecular skeleton with extensive π electron delocalisation together with chromophoric nature resulting from it, low solubility, high thermal stability, electrochromism, sublimability etc. [2–5]. A significant amount of work has been carried out for their magnetic and catalytic properties and also for their role in biomolecular processes [6,7].

Recently, porphyrazines as a congener of tetrapyrrols with an identical 16-membered core as in the case of phthalocyanines have been receiving increasing attention [8,9]. The structure–property relationship of these materials in their redox properties, conductivity and photoconductivity render them promising within a number of devices and also for singlet oxygen production in PDT [10].

While porphyrazines substituted with long alkyl or alkyloxy chains result in suitable soluble products for applications in liquid crystals and LB (Langmuir–Blodgett) layers, fusion of heterocyclic or macrocyclic units onto the core enables one to tune or enhance certain physical properties [11,12]. In this context, we might cite metal ion induced aggregation behaviour of crown ether substituted porphyrazines or supramolecular interactions in the case of pyridino-porphyrazines [13,14]. They have been used in the assembly of LB layers and ladder polymers and oligomers [15]. Bryce and co-workers [16] have applied porphyrazine in supramolecular chemistry by synthesising pyrazinoporphyrazines with pendant TTF (tetrathiafulvalene) units. We have been heavily engaged in the synthesis of novel porphyrazines carrying functional substituents such as dimethylamino [17], tosylamino [18], crown ether [19] or ferrocene moietes [20] through alkyl chains and these soluble products added novel functions to their physico-chemical properties. We have also prepared an unsymmetrically substituted phthalocyanine–porphyrazine hybrid capable of binding $PdCl_2$ on the periphery [21].

* Corresponding author. Tel.: +90-212-285-6827; fax: +90-212-285-63-86.
E-mail address: ahmetg@itu.edu.tr (A. Gül).

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Recently, intense research work has been carried out on tetrapyrrol macrocycles obtained by the replacement of benzo-groups in the phthalocyanine skeleton by heterocyclic rings similarly annulated to the porphyrazine core [12]. In this context, five-membered S and Se containing heterocycles, namely thiadiazole and selenodiazole, were annulated on the pyrrole rings in order to see the influence of these electron-rich and soft atoms on the electronic properties of the entire macrocycle [22–24]. In another work, tetrakis-2,3-(5,7-diphenyl-6H-1,4-diazepino) porphyrazine and its metal complexes were investigated for the planarity of the molecule after fusion of the seven-membered ring together with eight phenyl groups [12]. Pullen et al. [25] focused on porphyrazines with seven-membered heterocyclic rings carrying an O or S group in the 5-position. Tetrathienoporphyrazines were prepared as thiophene analogues of phthalocyanines and synthetic difficulties encountered were reported in detail [26]. Our earlier paper reporting a magnesium porphyrazine with 1,3-dithiol-2-thione heterocycle fused to the pheriphery is another example of heterocycle substituted porphyrazines with phthalocyanines [27].

In the present paper we report on the preparation of two different porphyrazine macrocycles having 1,4-dithiahexene units annulated to the pyrrol groups. The starting dicyano derivatives, in which the unsaturated dicyano-group is directly bound to sulfur atoms in a six-membered ring, have been previously reported [28–30].

2. Experimental

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer using KBr pellets, electronic absorption spectra on a Unicam UV–Vis spectrophotometer. Elemental analyses were carried out by the Instrumental Analysis Laboratory of TÜBİTAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using $SiMe_4$ as a reference. The metal content of some complexes were determined with a Perkin–Elmer Zeeman 3030 AA spectrometer in solution prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) mixture followed by dilution. Mass spectra were recorded on a VG Zab-Spec spectrometer.

*2.1. Synthesis of 6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyran-2,3-dicarbonitrile (**1**)*

To a stirred solution of 3.68 ml (0.0405 mol) dihydropyran and 8.85 g (0.027 mol) $K_3Fe(CN)_6$ dissolved in 40 ml distilled water was added over a 40 min period a solution of 2.5 g (0.0135 mol) dithiomaleonitril disodium salt dissolved in 40 ml distilled water at 0 °C. A red-orange colour developed during the reaction and a brown tarry material formed. The reaction mixture was extracted with diethyl ether, the etheral phase was dried over anhydrous sodium sulfate and then the solvent was evaporated to dryness. The residue was dissolved in a minimum amount of acetone (ca. 1 ml) and it was added dropwise into cool hexane (70 ml). After 15 min of stirring, the mixture was filtered and the precipitate was recrystallised from diethyl ether and dried in vacuo. Yield: 1.13 g, 37.5%. Mp 105 °C. *Anal.* Calc. for $C_9H_8N_2OS_8$: C, 48.21; H, 3.57; N, 12.5. Found: C, 47.95; H, 3.87; N, 12.32%. IR (KBr), ν(cm^{-1}): 2978, 2902, 2876, 2238, 2212, 1523, 1446, 1344, 1165, 1140, 1063, 1038, 910, 834, 706, 553, 502, 476. ^{1}H NMR (d-chloroform, 250 MHz): 5.76 (s, 1H, Ha); 4.06 (m, 1H, Hb); 3.73 (t, 1H, He); 3.49 (t, 1H, Hf), 2.04 (m, 2H, Hc); 1.92 (m, 2H, Hd). Mass spectrum (CI), $(MH)^+$ 225.

*2.2. Synthesis of tetrakis-[(6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyrano)]porphyrazinato magnesium (**MgPz1**)*

6 mg (0.25 mmol) Mg powder was dissolved by refluxing overnight in 5 ml of BuOH with the addition of a few crystals of I_2. To the magnesium butoxide suspension formed, 100 mg (0.5 mmol) **1** was added and after refluxing for 8 h under N_2 a dark blue suspension was obtained. The mixture was cooled to room temperature and then filtered. After the precipitate was refluxed in 50 ml THF for 4 h, it was filtrated and the filtrate was evaporated to dryness. The crude residue was washed first with methanol and then with *n*-hexane and dried in vacuo. Yield: 58 mg, 56.53%. Calc. for $C_{36}H_{32}N_8O_4S_8$ Mg: C, 46.96; H, 3.48; N, 12.17. Found: C, 47.22; H, 3.55; N, 11.92%. IR (KBr), ν(cm^{-1}): 2953, 2876, 1472, 1319, 1242, 1089, 1063, 1038, 910, 808. ^{1}H NMR (d_5-pyridine, 250 MHz): 6.17 (br s, 1H, Ha); 4.29 (br s, 1H, Hb); 4.02 (br s, 1H, He); 3.82 (br s, 1H, Hf); 2.21 (br s, 2H, Hc); 1.99 (br s, 2H, Hd). UV–Vis λ_{max}(nm) ($\log\varepsilon$) in THF: 662 (4.48), 522 (3.74), 370 (4.44).

*2.3. Synthesis of tetrakis-[(6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyrano)]porphyrazin (**H_2Pz1**)*

100 mg (0.446 mmol) **MgPz1** was demetallised by treatment with 5 ml of CF_3COOH at 25 °C for 1 h and then adding the mixture dropwise into an ice-water mixture (40 g). It was then filtered, washed first with water, then with MeOH, and then with diethylether and dried in vacuo. Yield: 47.5 mg, 48.66%. Calc. for $C_{36}H_{34}N_8O_4S_8$: C, 48.11; H, 3.79; N, 12.47. Found: C, 48.35; H, 3.52; N, 12.65%. IR (KBr), ν(cm^{-1}): 3298, 2927, 2876, 1497, 1319, 1242, 1063, 1038, 885, 808, 757. UV–Vis λ_{max}(nm) ($\log\varepsilon$) in THF: 702 (3.55), 622 (3.43), 517 (3.45), 357 (3.79). Mass spectrum (CI), $(M)^+$ 898.5.

*2.4. Synthesis of tetrakis-[(6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyrano)] porphyrazinato zinc (**ZnPz1**)*

100 mg (0.11 mmol) **H_2Pz1** was refluxed with 131.5 mg (0.5 mmol) Zn(acac)$_2$ (acac = 2,4-pentanedionate) in 50 ml THF for 24 h. After filtration of the mixture, the filtrate was evaporated to dryness. The crude product was washed first with methanol and then diethylether and finally dried in vacuo. Yield: 50 mg, 46.72%. Calc. for $C_{36}H_{32}N_8O_4S_8Zn$: C, 44.94; H, 3.32; N, 11.65. Found: C, 44.72; H, 3.48; N, 11.48%. IR (KBr), ν(cm^{-1}): 2953, 2876, 1498, 1319, 1242, 1089, 1063, 1038, 987, 910, 805. ^{1}H NMR (d$_5$-pyridine, 250 MHz): 5.85 (br s, 1H, Ha); 3.95 (br s, 1H, Hb); 3.72 (br s, 1H, He); 3.44 (br s, 1H, Hf); 1.87 (brs, 2H, Hc); 1.65 (br s, 2H, Hd). UV–Vis λ_{max}(nm) (log ε) in THF: 662 (4.24), 528 (3.60), 366 (4.20).

*2.5. Synthesis of tetrakis-[(6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyran)] porphyrazinato copper octakis copper acetylacetonate (**CuPz1.8[Cu(acac)$_2$]**)*

100 mg (0.11 mmol) **H_2Pz1** was refluxed with 316 mg (1.2 mmol) Cu(acac)$_2$ in 50 ml of THF for 2 days. After filtration, the filtrate was evaporated to dryness. The crude product was washed first with methanol then with diethylether and dried in vacuo. Yield: 43 mg, 12.63%. *Anal.* Calc. for $C_{116}H_{144}N_8O_{36}S_8Cu_9$: C, 45.61; H, 4.71; N, 3.67; Cu, 18.72. Found: C, 45.89; H, 4.31; N, 4.19; Cu, 18.38%. IR (KBr), ν(cm^{-1}): 2953, 2876, 2902, 1574, 1523, 1446, 1370, 1293, 1089, 1063, 1038, 935, 808. UV–Vis λ_{max}(nm) (log ε) in THF: 660 (4.05), 517 (3.75), 353 (4.16).

*2.6. Synthesis of 5-ethoxy-5,6-dihydro-[1,4]dithiino-2,3-dicarbonitrile (**2**)*

While 2.5 g (0.0135 mol) dithiomaleonitril disodium salt and 3.86 ml (40.5 mmol) ethyl vinyl ether were being stirred in 40 ml CH_3CN in an ice bath, a solution of 1 ml (0.0135 mol) $SOCl_2$ in 9 ml CH_3CN was added over 30 min. After filtration of the mixture, the filtrate was evaporated to dryness. The crude product was refluxed with active coal in 50 ml CH_2Cl_2 for 2 h, and then filtered while hot. When the filtrate was cooled to room temperature, **2** was crystallised. Yield: 800 mg, 28%. *Anal.* Calc. for $C_8H_8N_2OS_2$: C, 45.28; H, 3.77; N, 13.20. Found: C, 45.42; H, 3.57; N, 13.12%. IR (KBr), ν(cm^{-1}): 2978, 2953, 2902, 2238, 2212, 1523, 1421, 1344, 1319, 1217, 1191, 1165, 1089, 1038, 987, 961, 731, 655, 604. ^{1}H NMR (d-chloroform, 250 MHz): 5.37 (t, 1H, Ha); 3.99 (d, 1H, Hb); 3.60 (d, 1H, Hc); 3.32 (q, 2H, Hd); 1.30 (t, 3H, He).

*2.7. Synthesis of tetrakis-(5-ethoxy-5,6-dihydro-[1,4]dithiino)-porphyrazinato magnesium (**MgPz2**)*

6 mg (0.25 mmol) Mg powder was refluxed overnight in 5 ml of BuOH with the addition of a few crystals of I_2. To this mixture, 100 mg (0.471 mmol) **2** was added and the mixture was refluxed for 8 h under N_2. A dark blue suspension was obtained. It was filtered and the filtrate was evaporated to dryness. An oily residue was precipitated when it was treated with *n*-hexane at 0 °C. The precipitate was filtered and dried in vacuo. Yield: 68 mg, 76.43%. *Anal.* Calc. for $C_{32}H_{28}N_8O_4S_8Mg$: C, 44.24; H, 3.23; N, 12.90. Found C, 44.38; H, 3.51; N, 12.75%. IR (KBr), ν(cm^{-1}): 2978, 2953, 2876, 1727, 1472, 1293, 1268, 1114, 1063, 1038, 960, 936, 808, 757. ^{1}H NMR (d$_5$-pyridine, 250 MHz): 5.50 (br s, 1H, Ha); 3.78 (br s, 1H, Hb); 3.49 (q, 2H, Hd); 3.20 (br s, 1H, Hc); 0.94 (t, 3H, He). UV–Vis λ_{max}(nm) (log ε) in THF: 660 (4.53), 369 (4.54).

*2.8. Synthesis of tetrakis-(5-ethoxy-5,6-dihydro-[1,4]dithiino)-porphyrazin (**H_2pz2**)*

100 mg (0.5 mmol) **MgPz2** was demetallised by treatment with 5 ml of CF_3COOH at 25 °C for 1 h and then adding the mixture dropwise into ice-water (40 g). It was then filtered, washed first with water, then with MeOH, and then with diethylether and dried in vacuo. Yield: 47.5 mg, 48.45%. *Anal.* Calc. for $C_{32}H_{30}N_8O_4S_8$: C, 45.39; H, 3.55; N, 13.24. Found: C, 45.63; H, 3.40; N, 13.05%. IR (KBr), ν(cm^{-1}): 3298, 2953, 2851, 1497, 1310, 1063, 1038, 961, 808, 755. UV–Vis λ_{max}(nm) (log ε) in THF: 699 (3.97), 531 (4.10), 353 (4.27).

*2.9. Synthesis of tetrakis-(5-ethoxy-5,6-dihydro-[1,4]dithiino)-porphyrazinato zinc (**ZnPz2**)*

100 mg (0.11 mmol) **H_2Pz2** was refluxed with 131.5 mg (0.5 mmol) Zn(acac)$_2$ in 50 ml THF for 24 h. After filtration, filtrate was evaporated to dryness. The crude product was washed with methanol and *n*-hexane and dried in vacuo. Yield: 56 mg, 52.33%. *Anal.* Calc. for $C_{32}H_{28}N_8O_4S_8Zn$: C, 42.13; H, 3.07; N, 12.28. Found: C, 42.28; H, 3.27; N, 12.05%. IR (KBr), ν(cm^{-1}): 2928, 1498, 1421, 1038, 961. UV–Vis λ_{max}(nm) (log ε) in THF: 661 (4.26), 533 (3.70), 365 (4.27).

*2.10. Synthesis of tetrakis-(5-ethoxy-5,6-dihydro-[1,4]dithiino)-porphyrazinato copper octakis copper acetylacetonate (**CuPz2.8[Cu(acac)$_2$]**)*

100 mg (0.11 mmol) **H_2Pz2** was refluxed with 316 mg (1.2 mmol) Cu(acac)$_2$ in 50 ml THF for 2 days. After filtration, the filtrate was evaporated to dryness. The crude product was washed first with methanol, then with diethylether and dried in vacuo. Yield: 37 mg, 10.39%. *Anal.* Calc. for $C_{112}H_{152}N_8O_{36}S_8Cu_9$: C, 44.61; H, 5.04; N, 3.71; Cu, 19.02. Found: C, 43.06; H, 4.14; N, 3.15; Cu, 18.50%. IR (KBr), ν(cm^{-1}): 2978, 2927, 2902, 1574, 1523, 1446, 1395, 1319, 1089, 1062, 1038, 961, 706, 655, 629, 476. UV–Vis λ_{max}(nm) (log ε) in THF: 659 (4.09), 524 (3.85), 351 (4.23).

3. Electrochemical measurements

CV was carried out with a Princeton Applied Research Model 273 potentiostat/galvanostat controlled by an external PC using the computer program HEADSTRT and utilising a three electrode configuration at 25 °C. An Origin 6.0 graph program was used to evaluate HEADSTRT data, to draw voltammograms, and to analyse them. A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge containing saturated KCl adjacent to the SCE and solvent and carrier adjacent to the solution. Ferrocene was used as an internal reference, and potentials are also reported in Table 1 with respect to the Fc/Fc^+ redox potential in DCM. The working electrode was a Pt plate with an area of 1.0 cm^2. The surface of the working electrode was polished with a H_2O suspension of Al_2O_3 before each run. The last polishing was done with a particle size of 50 nm. Electrochemical grade tetrabutyl ammonium perchlorate (TBAP) in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.1 mol dm^{-3}. High purity N_2 was used for deaeration and to maintain a nitrogen blanket for at least 15 min prior to each run. During voltammetric measurements, the reference electrode tip was moved as close as possible to the working electrode so that uncompensated resistance of the solution was a smaller fraction of the total resistance, and therefore the potential control error was low. However, IR compensation was applied to the CV scans to further minimise the potential control error.

4. Results and discussion

As in the case of almost all synthetical procedures leading to porphyrazines, we need to start with unsaturated 1,2-dinitriles with heterocyclic units directly fused to these functional groups. Among many compounds which might be considered in this context, two dithiin derivatives, namely 6,7,8,8a-tetrahydro-4aH-[1,4]dithiino-[2,3-b]pyran-2,3-dicarbonitrile (**1**) and 5-ethoxy-5,6-dihydro-[1,4]dithiino-2,3-dicarbonitrile (**2**), have been preferred and the reactions to obtain these compounds were reported in detail by Simmons et al. [29,30]. Essentially, the disodium salt of dithiomaleonitrile was first oxidised to an intermediate, which could function similar to a diene component in a Diels–Alder addition with vinyl ether during the second stage of oxidation. The oxidant-vinyl ether couples used to obtain **1** and **2** are potassium ferricyanide-dihydropyran and thionyl chloride-ethyl vinyl ether, respectively. The work-up procedures have been modified to obtain the products with a yield of about 30% (Fig. 1).

The cyclotetramerisation process with either of the dinitrile derivatives **1** or **2** in the presence of magnesium butanolate was observed to be the only way to synthesise the corresponding magnesium porphyrazinate derivatives **MgPz1** or **MgPz2** in butanol. Treatment of these magnesium compounds with a strong organic acid,

Table 1
Cyclic voltammetric parameters of the compounds

Compound	Redox process	[a]$E_{1/2}$ (V)	ΔE_p (mV)	$\delta E_p/\delta \log v$ (mV)	$I_{p,a}/I_{p,c}$	αn	[b]$D \times 10^{12}$ m^2 s^{-1}
H_2Pz1	Ic/Ia	−0.367	65	30	1.02	1.0	6.62
	IIc/IIa	−0.780	85	38	0.72	0.83	
	IIIc/IIIa	−1.193		103		0.29	
H_2Pz2	Ic/Ia	−0.385	67	32	0.98	0.94	9.21
	IIc/IIa	−0.805	74	48	0.69	0.63	
	IIIc/IIIa	−1.212		116		0.26	
MgPz1	Ic/Ia	−0.673	78	23	1.09	0.96	5.40
	IIc/IIa	−1.097	67	42	0.67	0.71	
	IIIc/IIIa	−1.351		64		0.47	
MgPz2	Ic/Ia	−0.696	76	30	0.89	1.0	9.81
	IIc/IIa	−1.136	81	34	0.66	0.89	
	IIIc/IIIa	−1.374		67		0.45	
ZnPz1	Ic/Ia	−0.618	75	33	0.96	0.93	5.65
	IIc/IIa	−1.025	31	50	0.71	0.60	
	IIIc/IIIa	−1.312		53		0.56	
ZnPz2	Ic/Ia	−0.655	67	30	0.90	1.0	8.41
	IIc/IIa	−1.098	86	37	0.67	0.81	
	IIIc/IIIa	−1.350		68		0.44	

[a] For irreversible processes $E_{p,c}$ is given.

[b] D is calculated by using the slope of the line obtained from the graph, $I_{p,c}$–$v^{1/2}$ ($I_{p,c}$ is the first cathodic peak current) and the expression; $I_p = -(2.69 \times 10^5)An^{3/2}C_0D^{1/2}v^{1/2}$.

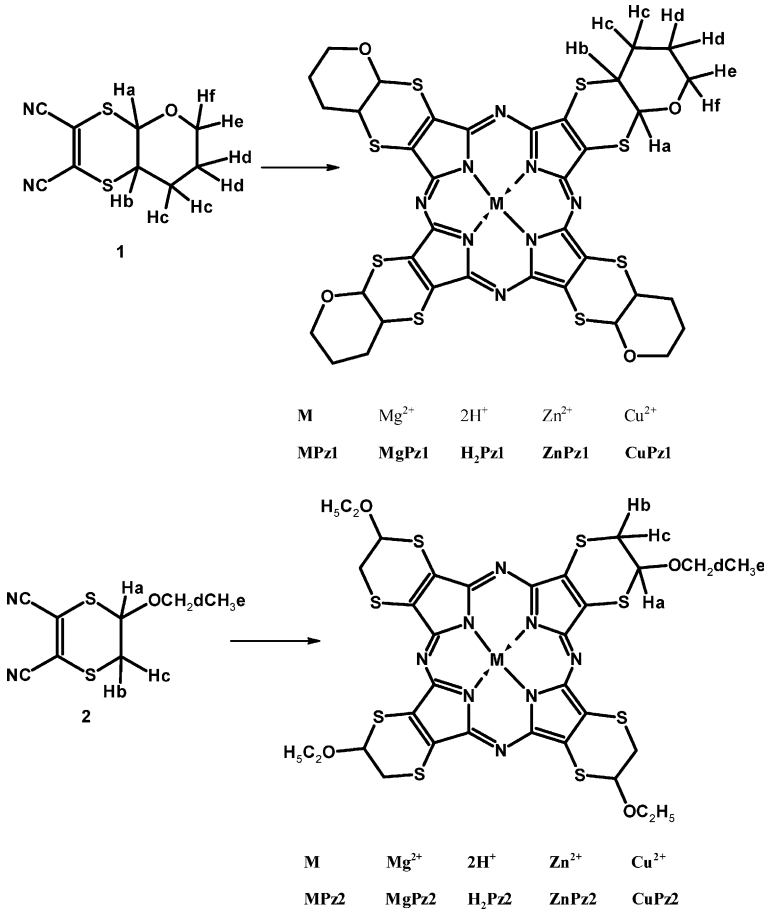

Fig. 1. Discarbonitriles **1** and **2** and the porphyrazines derived from them.

e.g., trifluoroacetic acid, at room temperature for 2 h afforded the metal-free derivatives **H_2Pz1** and **H_2Pz2**. Apparent differences between magnesium and metal-free derivatives are the change of colour from dark blue to purplish blue and lowering in the solubility. Insertion of metal ions into metal-free derivatives has been proven to be the only route to further metallise these macrocycles [31]. A range of conditions for the conversion of metal-free porphyrazines, **H_2Pz1** and **H_2Pz2** into copper and zinc complexes was investigated [11,17–20]. However, even using the optimum conditions which involved treatment with anhydrous Cu(II) and Zn(II) salts in refluxing solvents or solvent mixtures including chloroform, methanol, THF, etc. for long periods, we could not isolate appreciable amounts of well characterised metal-porphyrazine derivatives. With the aim of having a soluble metal reactant, acetylacetonate (acac) complexes of Cu(II) and Zn(II) were tried satisfactorily. The products were the desired metallo porphyrazines; however, elemental analysis results indicated that an additional eight $Cu(acac)_2$ units are present in the case of both **CuPz1** and **CuPz2**.

FTIR spectra clearly indicate the presence of the proposed functional groups at 2978, 2953 (CH), 2238, 2212 (CN), 1063, 1038 (CO) for **1** and 2953, 2902, 2876 (CH), 2238, 2212 (CN), and 1089, 1063, 1038 (CO) for **2** as intense absorptions. Cyclotetramerisation of the dinitriles was confirmed by the disappearance of the sharp C≡N vibrations at 2238 and 2212 cm^{-1}. The NH groups in the inner core of the metal-free derivatives **H_2Pz1** and **H_2Pz2** gave an absorption at 3298 cm^{-1} [18–20]. **CuPz1** and **CuPz2** show additional absorption peaks when compared with the other metal porphyrazines; these are intense absorptions around 1574 and 1523 cm^{-1} which are typical for metal acetylacetonate derivatives [32]. These data provide additional evidence for the presence of attached copper acetylacetonate units on the porphyrazine macrocycles. The ^{1}H NMR spectra are also consistent with the proposed structures. In compound **1**, two CH protons appear at the lower field as a singlet at 5.76 and a multiplet at 4.10 ppm. Three methylene protons come out at 3.49, 2.04 and 1.92 ppm. In compound **2**, the CH proton is a triplet at 5.37 ppm and the methylene protons of the heterocycle a doublet at 3.99 and 3.60 ppm. The ethoxy group shows the two signals at 3.32 and 1.30 ppm. Due to the insolubility of the porphyrazine products, their ^{1}H NMR spectra could be taken only in solvents such as

pyridine and DMSO. Consequently, the spectra are rather broad because of the solvent effect. The most revealing data for a tetrapyrrol system are given by their UV–Vis spectra in solution. The electronic absorption spectra of the metal-free porphyrazines **H_2Pz1** and **H_2Pz2** exhibited a splitted Q band absorption which is due to π–π^* transitions of these completely conjugated 18-π electron systems. The consequence of the lower symmetry introduced by variations of the substituents on the periphery was hardly observed as a shoulder at the lower energy side of the intense Q bands, so the characteristic Q band transitions of the metal porphyrazinates were observed as a single band of high intensity. The effect of eight S-substituents on the periphery of the porphyrazine core was a shift in these intense Q bands to longer wavelengths when compared with those of unsubstituted or alkyl substituted derivatives [33]. Among the metal porphyrazinates, the Q band absorption of Cu(II) derivatives (**CuPz1** and **CuPz2**) show a clear difference from the others with a rather broad peak in the red region. Together with the other spectral and physical evidences, we might accept this as a further confirmation of the coordination of copper acetylacetonate units to peripheral sulfur-donors.

5. Electrochemical results

To further test the effect of the metal centre and the ring substituents on the electrochemical behaviours of porphyrazine derivatives, their electrochemistry was investigated by using cyclic voltammetry. The reduction and oxidation behaviours of metaloporphyrazine derivatives are due to the interaction between the ring and the metal centre [34,35]. Metalloporphyrazine derivatives typically show two ring oxidations, up to four ring reductions and redox processes of the electroactive metal centre and substituents [31,36–40]. The first two reductions are usually reversible and the other reduction and oxidation processes are not. Each complex (except Cu derivatives) investigated in this study also shows two reversible and an irreversible process that can be attributed to the ring-centred reductions. Within the limit allowed by the DMSO/TBAP solvent system (+1.0 V), no oxidation processes are observed (Table 1). First-row transition metal porphyrine, phthalocyanine and porphyrazine complexes differ from those of the main-group metal complexes due to the fact that metal "d" orbitals may be positioned between the HOMO and LUMO of the porphyrine, phthalocyanine, or porphyrazine rings [31,37,39–43]. According to these studies, the first oxidation and the first reduction processes occur on the metal centre in the metal complexes only for Mn, Fe and Co derivatives. For Ni, Cu and Zn derivatives, redox processes take place on the ring. As

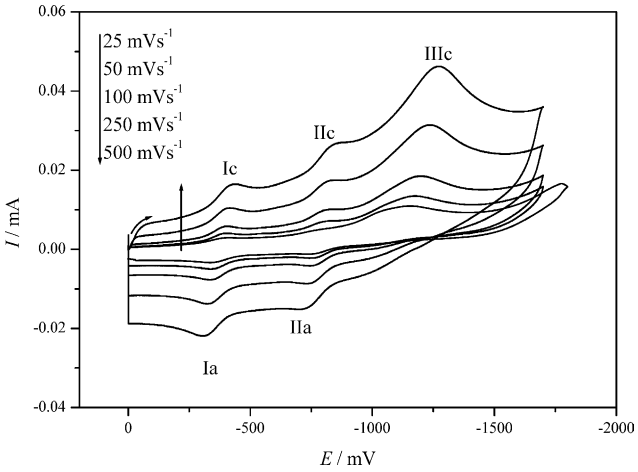

Fig. 2. Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} **H_2Pz1** in 0.1 mol dm^{-3} TBAP + DMSO vs. SCE.

representative of the compounds studied here, the electrochemical behaviours of **H_2Pz1** is analysed in detail. Within the accessible potential range of the DMSO/TBAP solvent system, **H_2Pz1** exhibits three reduction waves at about −0.367, −0.780 and −1.193 V at a scan rate of 0.10 V s^{-1} vs. SCE (Fig. 2). Cyclic voltammetric data of this compound as well as all the other compounds studied here are given in Table 1. The variations of the peak separations (ΔE) with the scan rate and $E_p/\log v$ values are used to identify the reversibility of a redox process [37,39,44–46]. The $E_p/\log v$ value of the Ic/Ia redox couple is 30 mV. ΔE of this couple is 65 mV at 0.100 V s^{-1} and increases slightly with the increasing scan rates. The reversible nature of this electrode process at lower scan rates is unambigous; at higher scan rates, although a peak-to-peak separation slightly departing from 59 mV might be considered diagnostic of "quasi-reversibility", such minor departure is generally due to uncompensated solution resistance. The IIc/IIa couple has also similar reversibility to the Ic/Ia one as understood from the $E_p/\log v$ and the ΔE values of this couple. The IIIc process does not give the anodic couple during the reverse scan and has a very high $E_p/\log v$ (103) value indicating irreversible properties of the process. The plot of the peak current ($I_{p,c}$) vs. the square root of the scan rate ($v^{1/2}$) for Ic and IIc redox processes of **H_2Pz1** give straight lines revealing diffusion-controlled mass transfer mechanism of the processes. However, the peak current ($I_{p,c}$) of the IIIc is not directly proportional to the square root of the scan rate ($v^{1/2}$), so process III is not diffusion controlled.

Fig. 3 shows the change in the ratio of the anodic to the cathodic peak current ($I_{p,a}/I_{p,c}$) as a function of the scan rate. In the case of the Ic/Ia redox process of **H_2Pz1**, the $I_{p,a}/I_{p,c}$ ratio is unity and does not change with increasing scan rate, indicating a simple electron transfer mechanism. The $I_{p,a}/I_{p,c}$ ratios of the IIa/IIc redox process decrease with increasing scan rate sug-

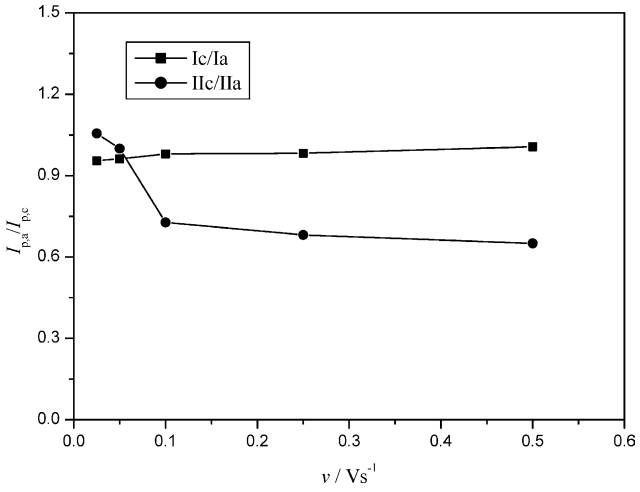

Fig. 3. Change in the anodic to cathodic peak current ratio ($I_{p,a}/I_{p,c}$) with scan rate (v) for **H_2Pz1**.

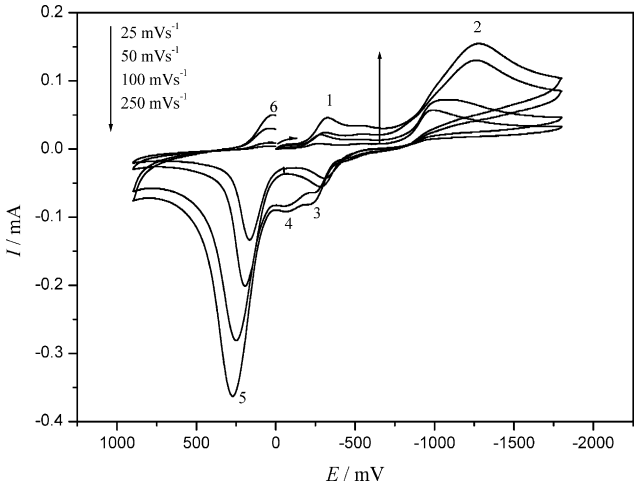

Fig. 4. Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} **CuPz1** in 0.1 mol dm^{-3} TBAP + DMSO vs. SCE.

gesting the existence of a reversible chemical reaction following this electron transfer process.

The general appearance of the voltammograms obtained for metallo-compounds **MgPz1** and **ZnPz1** is substantially similar to that of **H_2Pz1**. When the voltammetric data of the metal-free derivatives are compared with those of metallo-compounds one could easily conclude that the complexation of the free porphyrazine ligand with different metal ions shift the reduction processes towards negative potentials (approximately 0.300 V) and also change the electron transfer potentials. Effect of the peripheral substituents on the electrochemical behaviour of the porphyrazine derivatives are investigated by comparing the electrochemical behaviour of the compounds denoted by **MPz1** with those by **MPz2**. The general appearance of the voltammograms is similar as expected and the main difference is the shift of the reduction reactions towards more negative potentials in compounds **MPz2** than those of **MPz1**, as a result of their electron donating properties.

The electrochemical behaviour of copper porphyrazines studied here shows some peculiarities in parallel with the other spectral findings. The voltammogram of **CuPz1** as presented in Fig. 4 is rather interesting and different than those of other metal-free and metal-porphyrazines. During the cathodic scan it gives two irreversible cathodic waves at −0.295 and −1.244 V and during the reverse scan, three peaks at −0.255, 0.064 and 0.246 V are recorded. As seen from the figure, wave 2 has a very high peak current with respect to peak 1 (approximately fourfold of peak 1) and it is very broad. This behaviour is more different than the common porphyrazine ring reduction processes. During the reverse scan wave 4 is recorded only at higher scan rates and peak 5 has an adsorption character as observed from its peak current change as a function of the scan rate. When we change the switching potential of the voltammograms, the complex shows very different voltammetric behaviours (Fig. 5). When the potential is switched before peak 2, only peaks 1 and 5 are recorded and peak 5 has a diffusion-controlled character. When peak 2 is also included, peaks 3 and 4 start to appear during the reverse scan and the peak current of 5 increases as a function the switching potential. This means that only after potentials more negative than $E_{p,c}$ of peak 2 do peaks 3 and 4 appear and the mass transport mechanism of peak 5 turns into adsorption character. These different and interesting behaviours can be a consequence of the structure of **CuPz1** which has eight additional Cu^{II} ions coordinated to the substituents of the porphyrazine ring.

In the experiments to ascertain the reversibility of the Cu(II)/Cu(I) process, it has been observed that further reduction to the Cu(0) state occurs before −0.7 V and a typical anodic stripping due to the sudden reoxidation

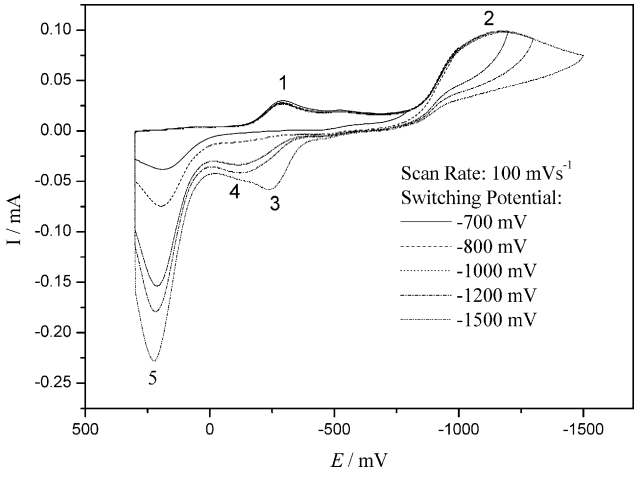

Fig. 5. Effect of switching potential to the cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} **CuPz1** in 0.1 mol dm^{-3} TBAP + DMSO vs. SCE.

of the electrodeposited copper metal appears during return peak 5. Consequently, the processes occurring at peak 2 are simply due to the multiple reductions of the porphyrazine ring at a nominally copper electrode.

CuPz2 shows similar voltammetric behaviour to **CuPz1**. It gives also two reduction peaks at −0.290 and −1.271 V during the cathodic scan and three anodic peaks during the reverse scan at −0.292, −130 and 0.268 V. The high peak current and the broad shape of peak 2 signify the demetallation of the complexes during this process. Peak 5 has also adsorption properties and is effected as the switching potential. Peak 6 in Fig. 4 corresponds to the reduction of Cu^{2+} ions originating from the stripping process in peak 5 and its intensity depends on the scan rate. These different voltammetric responses of the copper porphyrazines provide further confirmation of the structures proposed according to the other spectral results.

Acknowledgements

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