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# Synthesis, characterization and spectroscopic investigation of novel tetra-(1,4-dithiin)porphyrazine network polymers derived from dithianone monomer

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## ABSTRACT

Chloranil through condensation reaction with di (sodiothio)maleonitrile produced heterocyclic dithianone monomer, p-benzoquinonebis[2,3-b; 2‘,3‘-b‘]1,4-dithiin-2,3-dinitrile. The tetranitrile monomer was cyclo-tetramerised using lithium/pentanol and acetic acid affording the corresponding tetra p-benzoquinone bis[2,3-b; 2‘,3‘-b‘] (1,4-dithiin)porphyrazine)]-based network polymer (2H-Pz). The tetranitril monomer was cyclo-tetramerised using metal salt and quinoline affording the corresponding tetra p-benzoquinonebis[2,3-b; 2‘,3‘-b‘](1,4-dithiin)porphyrazinato-metal II-based network polymers (M-Pz), M = Co, Ni or Cu. Elemental analytical results, IR and NMR spectral data of the prepared molecules are consistent with their assigned formulations. Molecular masses and metal contents of the synthesized polymers confirm the efficiency of tetramerization polymerization and complexation reactions.

## KEYWORDS

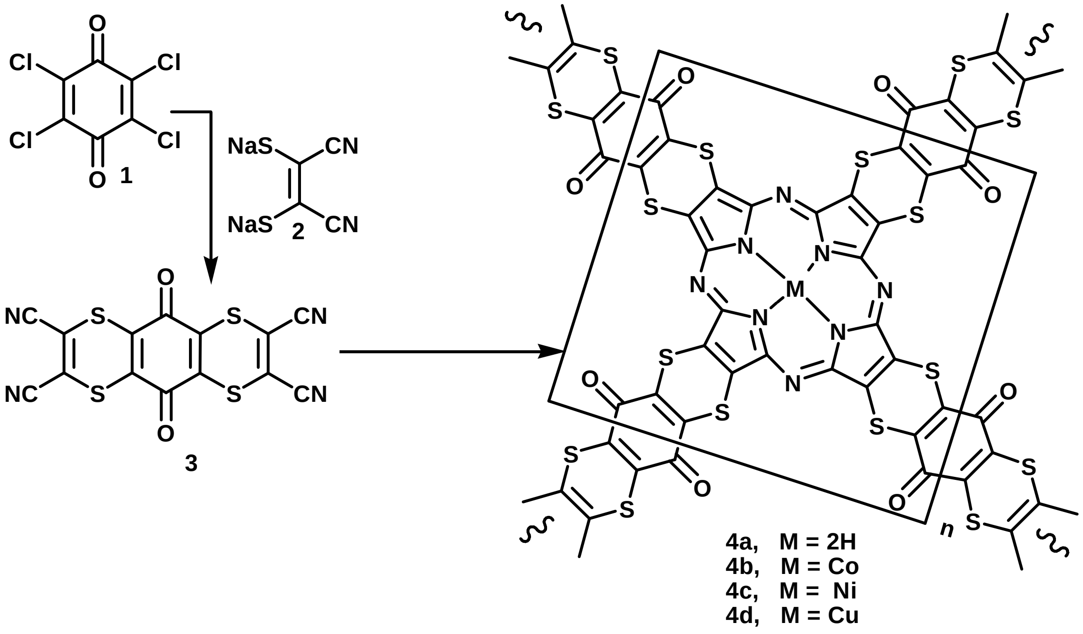
Sulfur-containing metal (II) porphyrazine;
dithianone.

## INTRODUCTION

Tetra-(1,4-dithiin)porphyrazine is one of the phthalocyanine derivatives having two sulfur atoms at equivalent 1,4-positions of the phthalocyanine benzene units. Due to the additional sulfur atoms, tetra (1,4-dithiin)porphyrazines are less electron-rich than the corresponding phthalocyanine[1]. Porphyrazine complexes of zinc, aluminium or other metals show anticancer properties and uses in photodynamic therapy[2]. The novel tetra-(1,4-dithiin) metal-free (H2-Pz) and metalloporphyrazines (MPz, M = Mg, Fe) bearing peripheral tetrapropyl-bromine derived from 2,3-dicyano-5-propyl-bromine-1,4-dithiin and disodiomaleonitrile, were synthesized in a multi-step reaction sequence[3]. A novel catalyst iron (II) tetra (1,4-dithin)porphyrazine for oxygenating degradation of organic pollutants in aqueous solutions was reported[4]. Base-induced cyclotetramerisation of the aromatic dinitriles with magnesium butoxide in refluxing butanol generates the peripherally peralkynylated phthalocyanine or naphthalocyanine analogues, namely the tetrapyrazin oporphyrazines and tetra-6,7-quinoxalinoporphyrazines, respectively[5]. Synthesis and photocatalytic properties of iron (II)-tetramethyl-tetra (1,4-dithiin)porphyrazine were reported[6]. Metal-free and magnesium tetra-ester tetra (1,4-dithiin)porphyrazine were successfully synthesized.[7] Synthesis and photocatalytic properties of zinc (a!)-tetra (1,4-dithiin)porphyrazine bearing peripheral tetrapropyl-bromine were reported[8]. Microporous polymeric materials were prepared through double aromatic nucleophilic substitution reaction of appropriate hydroxylated aromatic monomers with 4,5-dichlorophthalonitrile yielding a bis (phthalonitrile) precursor that forms a phthalocyanine network, via a cyclotetramerization by a metal ion template[9,10]. Dielectric properties of new fully conjugated 2H- and metal-pyrazinoporphyrazine network polymers prepared from the readily derivatized diaminomaleonitrile (DAMN) with 2,7-di-tert-butylpyrene-4,5,9,10-tetraone[11]. Novel fully conjugated 2H- and metal-phthalocyanine network polymers were synthesized[12]. Chloranil through condensation reaction with 4-amino-3-methyl-1-phenyl-5-(hydroxyl, mercapto or imino)-pyrazole produced new cyanine dyes[13]. Synthesis, Characterization and Spectroscopic Investigation of Novel Pyrazino-porphyrazine Network Polymer-Supported Metal (II)-Based Catalysts[14]. The aim of this work is the synthesis of new metal free and metal (II) Tetra (1,4-dithiin)porphyrazine–based network polymers.

## RESULTS AND DISSCUSION

Chloranil through condensation reaction with di (sodiothio)maleonitrile produced dithianone heterocyclic monomer, p-benzoquinonebis[2,3-b; 2‘,3‘-b‘]1,4-dithiin-2,3-dinitrile 3, brown crystals, soluble in acetone, chlorobenzene and dioxane. The tetranitrile monomer 3 was cyclo-tetramerised10 using lithium/pentanol and acetic acid affording the corresponding tetra p-benzoquinone bis[2,3-b; 2‘,3‘-b‘](1,4-dithiin)porphyrazine)]-based network polymer (2H-Pz) 4a. The tetranitril monomer was cyclo-tetramerised10 using metal salt and quinoline affording the corresponding (1,4-dithiin)porphyrazinato-metal II-based network polymers (M-Pz), 4b-d, M = Co, Ni or Cu (scheme 1). Elemental analytical results, IR and NMR spectral data of the new prepared molecules are consistent with their assigned formulations. Molecular masses and metal contents of the synthesized polymers confirm the efficiency of tetramerization polymerization and complexation reactions. Despite their rigid structures[15] these polymers are freely soluble in some organic solvents, which allow an estimation of their low molecular masses.



Scheme 1

Owing to their low molecular weight, the prepared porphyrazines display good solubility in organic solvents, such as THF, ethyl acetate, acetone, dichloromethane, chloroform, dimethylformamide and dimethylsulfoxide.

## Infrared and UV-Vis spectrum

IR spectral data of precursor 3 shows an intense bands at 1615, 1689 and 2234 cm-1 assigned to C=C, C=O and Ca”N groups, respectively (Figure1). IR spectrum of metal free [1,4]dithiinoporphyrazine-based network polymer 2H-Pz 4a shows a broad band at 1517 cm”1, which is assignable to the stretching vibration of the C=N bond. The absorption values of the C=N vibration at 1504, 1506, and 1503 cm$^{”1}$ (see experimental) for Co-Pz 4b, Ni-Pz 4c and Cu-Pz 4d respectively, are lower by about 11-14 cm$^{”1}$ than those for the metal free 2H-Pz 4a, which indicate the coordination of azomethine nitrogen atom to metal ions in the complexes.

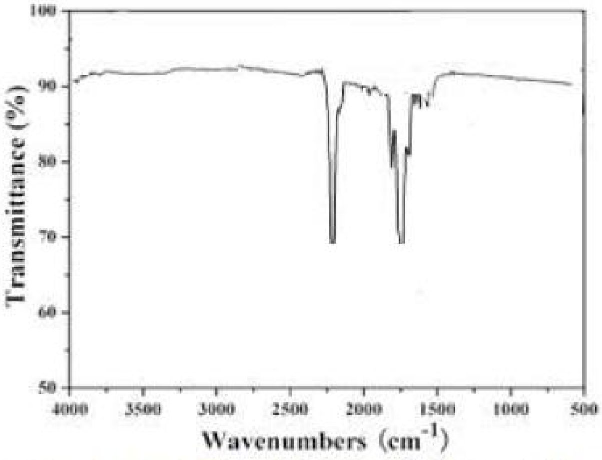


**Figure 1 : FT-IR spectrum of tetranitrile monomer 3**

Moreover, there is an extra broad band at 3354 cm$^{-1}$, assignable to the stretching vibration of the N-H bond in free metal (1,4-dithiin)porphyrazine complex 2H-Pz 4a. This stretching vibration of the N-H bond does not appear in the spectra of metal complexes 4b-d which means that NH group is involved in metal-ligand formation. UV-Vis spectrum of 2H-Pz 4a in dichloromethane solution shows a strong soret band at 353 nm (Figure 2). The Q bands attributable to the difference between the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy, that is, the $\pi$-$\pi$* transitions in 2H-Pz 4a are observed at 629, 708 nm. These bands are in a good agreement with the absorption spectra reported in the literature[16]. The electronic absorption spectra of the metal complexes 4b-d in dichloromethane solution are presented in Figure 2. Two transitions are dominated at higher-energy B-band (broad bands around 362 nm and shoulder bands around 423 nm) which can be assigned to the $\pi$-$\pi$* and/or d-$\pi$* transitions in the fused pyrolo (1,4-dithiin) ring structure[17,18] Two characteristic well developed intense lower-energy, Q-bands, (around 635 nm and 718 nm) are observed. The shoulder band is usually attributed to the 1s ’! 4d transition[19]. It was demonstrated already in early theoretical work[20,21] that exchange coupling of the metal center with ligand states gives rise to spin-allowed transitions at low energy. It will be shown that there are states in the range of 424-435 nm below the Q-band excitation for all of the metal-(1,4-dithiin)porphyrazine polymers. These states arise from d–d excitations and ligand–metal exchange coupling. There is a little difference among the visible spectra of various metal (1,4-dithiin)porphyrazines (Figure 2). It has been suggested that both Q and B bands can be influenced by the metal-to-ligand charge-transfer bands[22].It is clear that the absorption bands for metal complexes, extends beyond 800 nm. Thus, these (1,4-dithiin)porphyrazines could be useful in the field of optical data storage and for security printing which require absorbance in the near infrared.

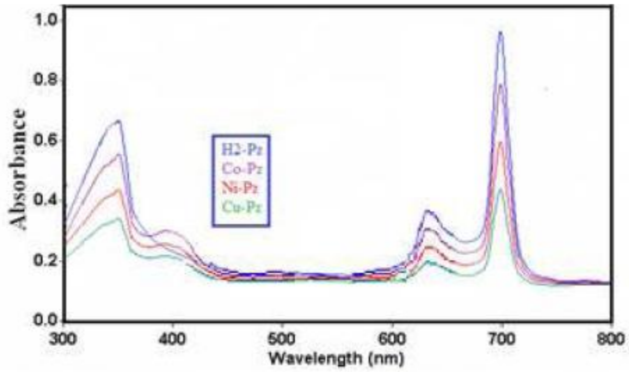


**Figure 2 : UV-Vis spectra of metal free- and metal-(1,4-duthiin)porphyrazine network polymer 4a-d**

## NMR and molecular mass measurements of the prepared compounds

In accordance with the structure of *p*-benzoquinone bis[2,3-b; 2‘,3‘-b‘]1,4-dithiine-2,3-dinitrile 3, the $^{13}$C

NMR spectrum (Figure 3) revealed bands at 115.7, 123.6, 158.3 and 178.4 assignable to CN, C=C (thiin ring), C=C (benzoquinone ring) and C=O, respectively. Elemental analytical results of new tetranitrile 3, is consistent with the assigned formulation (see experimental, scheme 1, figure 4). $^1$H-NMR spectrum of metal free (1,4-dithiin)porphyrazine-based network polymer 2H-Pz 4a reveals one signal at $\delta = 0.78$ assignable to NH protons (Figure 4). The presence of signal assignable to NH protons in $^1$H-NMR spectrum of 2H-Pz 4a gives direct evidence of the formation of an unsymmetrical tetradentate ligand. $^{13}$C NMR spectrum of 2H-Pz 4a (Fig. 5) revealed a small band at110.3 assignable to CN group and big bands at 117.4 (C), 120.2 (C), 122.6 (C), 128.2 (C), 129.8 (C), 155.6 (C), 158.4 (C), 160.4 (C) and 187.4 (C) which confirm the structure of the prepared polymer. From the results it should be regarded that the presence of small band assignable to cyano groups is attributed to the cyano groups found at the edges of the polymer indicating cyclotetramization. Elemental analyses of the prepared polymers show that the amount of carbon within the repeat unit of the polymers is consistent with their idealised structures represented in scheme 1. The experimental values of carbon content of the prepared polymers are consistent with that calculated for the expected polymer repeat unit. Also, the experimental values of metal content (see experimental) of the prepared polymers are consistent with that calculated for the expected polymer repeat unit. Moreover, metal content (see experimental) and molecular masses of the synthesized polymers confirm the efficiency of tetramerization polymerization and complexation reactions. BET surface areas of the prepared polymers are shown in TABLE 1. Nitrogen adsorption measurements show that the materials have high surface areas in the range 458–479 m$^2$g$^{-1}$ with very significant adsorption at low relative pressure (P/Po < 0.02) indicating microporosity[23]. Small differences have been observed in the metal-(1,4-dithiin)porphyrazines BET surface areas. Low molecular mass and the presence of voids in these materials which make them contorted represent an efficient way to prevent the aggregation and consequently obtain material with good solubility properties allowing conventional solution-based polymer processing techniques.

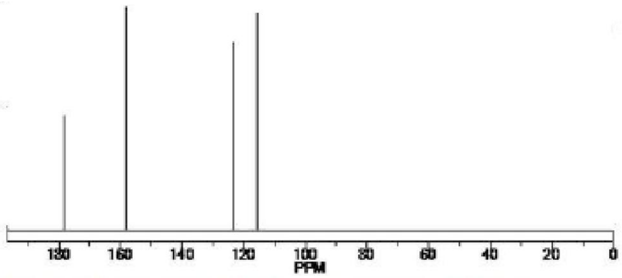


**Figure 3 : $^{13}$C NMR spectra of tetranitrile monomer in $CDCL_3$3**

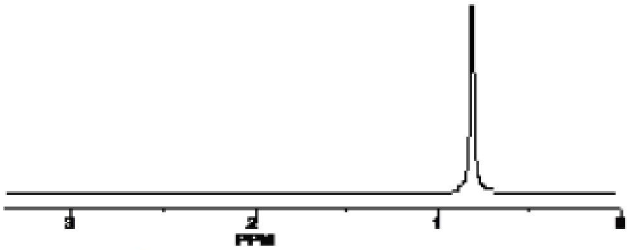


**Figure 4 : $^1$HNMR spectra of 2H-(1,4-dithiin)porphyrazine network polymer 4a in $CDCL_3$**

**TABLE 1 : Characteristic data of the prepared (1,4 dithiin) porphyrazine network polymers**

| No. | Sample | Yield (%) | Mp ($^o$C) | BET surace area (m$^2$/g) |
|---|---|---|---|---|
| 4a | 2H-Pz | 88 | 233-234 | 479 |
| 4b | Co-Pz | 82 | 208-209 | 458 |
| 4c | Ni-Pz | 89 | 225-226 | 463 |
| 4d | Cu-Pz | 86 | 212-213 | 465 |

## Thermal analysis

Thermal stability of the prepared network polymers was also examined. The results show that metal-free (1,4-dithiin)porphyrazine network polymer 4a has significantly comparable degradation temperature (Td) at 423 °C. However, metal-(1,4-dithiin)porphyrazine network polymers 4b-d show better thermal stability with a main degradation step taking place at 443 °C for Co-Pz, 448 °C for Ni-Pz and 445 °C for Cu-Pz.

## EXPRIMENTAL

## Characterization

Fourier-transform infrared spectrometer (8101 M-Shimadzu) was used in spectral measurements. UV-vis spectra were obtained using Unicam UV-Vis spectrometer. NMR spectra were recorded in deuterio-chloroform, on a Varian VXR 400S NMR spectrometer operating at 400 MHz (1H NMR) and 100 MHz ($^{13}$C NMR) with tetramethylsilane as internal standards. Elemental analysis for metal content was carried out by a Perkin–Elmer Analyst 300, AAS atomic absorption spectrometer. Elemental analyses were determined with Perkin-Elmer 2400 CHN. BET surface areas were calculated from the nitrogen adsorption isotherms at 77 K by using a Micromeritics ASAP 2000 surface analyzer.

### Synthesis of *p*-benzoquinonebis[2,3-b; 2‘,3‘-b‘]1,4-dithiine-2,3-dicarbonitrile 3

A mixture of unimolar ratio (0.01 mol) of *p*-chloranil 1 and bimolar ratio (0.02 mol) of di (sodiothio)maleonitrile 2 was heated in dimethylformamide (50 mL) at 80 °C for 8 h. The reaction mixture changed to brown at the end of the refluxing. It was filtered while hot, precipitated by ice water mixture collected, washed with water several times, dried and crystallized from ethanol.

88% yield (brown crystals); MP: 220 °C; IR (KBr): $\nu$ cm$^{-1}$, 1618 (C=C), 1697 (C=O), 2232 (CN); $^{13}$C NMR (CDCl$_3$) $\delta$ = 115.8, 123.6, 158.5, 178.2. Anal. calcd. for C14N4O2S4(Mol. Wt.: 384.44) requires: C, 43.74; N, 14.57 %. Found: C, 43.86; N, 14.69 %.

### Synthesis of tetra-*p*-benzoquinonebis[2,3-b; 2‘,3‘-b‘](1,4-dithiin)porphyrazine-based network polymer (2H-Pz) 4a

Lithium metal (20 mg, 2.8 mmol) was added to a refluxing solution of 3 (158.025 mg, 0.5 mmol) in pentanol (20 mL). The solution was heated at reflux for 16 h. On cooling, acetic acid (0.2 mL) was added to the reaction mixture and the crude product was collected by centrifugation. The green material was purified by column chromatography (eluent: dichloromethane) and precipitated from methanol.

IR (KBr): $\nu$ cm$^{-1}$, 1517 (C=N), 1613 (C=C), 1690 (C=O). 3354 (NH) UV-Vis $\lambda_{max}$ (CH$_2$Cl$_2$)/nm): 353, 629, 708. $^1$H NMR (CDCl$_3$) $\delta$ = 0.78 (s, NH). Anal.calcd. for the expected polymer repeat unit $C_{28}H_2N_8O_4S_8$ (Mol. Wt.: 770.89) requires: C, 43.63; H, 0.26; N, 14.54;%. Found: C, 43.77; H, 0.32; N, 14.68 %.

### Synthesis of tetra-*p*-benzoquinonebis[2,3-b; 2‘,3‘-b‘](1,4-dithiin)porphyrazinato-metal II-based network polymers (M-Pz) 4b-d

The tetranitrile monomer 3 (158.025 mg, 0.5 mmol) was subjected to form the corresponding polymer network on heating with 0.75 mmol of metal salt (cobalt chloride, nickel II chloride or copper nitrate) in quinoline (20 mL) at 200 ºC for 16 h. The material was dissolved in acetone, and the un-trapped metal was precipitated and removed from the solution. To the resulting acetone solution, an excess of cold methanol was added, precipitating dark green (4b, 4c) or blue (4d) solids which are easily purified by chromatography on silica gel (eluent: dichloromethane). The polymer was vacuum dried overnight.

**4b**: IR (KBr): $\nu$ cm$^{-1}$, 1504 (C=N), 1609 (C=C), 1686 (C=O). UV-Vis $\lambda_{max}$ (CH$_2$Cl$_2$)/nm): 354, 429 (shoulder), 643, 712. Anal. calcd. for the expected polymer repeat $C_{28}N_8O_4S_8$Co (Mol. Wt.: 827.8) requires: C, 40.63; N, 13.54; Co, 7.12 %. Found: C, 40.78; N, 13.71; Co, 7.03 %.

**4c**: IR (KBr): $\nu$ cm$^{-1}$, 1506 (C=N), 1612 (C=C), 1689 (C=O). UV-Vis $\lambda_{max}$ (CH$_2$Cl$_2$)/nm): 369, 423 (shoulder), 633, 719. Anal. calcd. for the expected polymer repeat $C_{28}N_8O_4S_8$Ni (Mol. Wt.: 827.56) requires: C, 40.64; N, 13.54; Ni, 7.09 %. Found: C, 40.81; N, 13.68; Ni, 7.20 %.

**4d**: IR (KBr): $\nu$ cm$^{-1}$, 1503 (C=N), 1607 (C=C), 1692 (C=O). UV-Vis $\lambda_{max}$ (CH$_2$Cl$_2$)/nm): 356, 418 (shoulder), 629, 724. Anal. calcd. for the expected polymer repeat $C_{28}N_8O_4S_8$Cu (Mol. Wt.: 832.42) requires C, 40.40; N, 13.46; Cu, 7.63 %. Found: C, 40.57; N, 13.57; Cu, 7.51 %

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## CONCLUSION

Chloranil through condensation reaction with di (sodiothio)maleonitrile produced heterocyclic tetranitrile monomer which was found to be useful in generation of new metal free- and metal- (1,4dithiin)porphyrazine network-polymers. Molecular mass, thermal stability and good solubility of these polymers allow conventional solution-based polymer processing techniques.

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