

## SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC INVESTIGATION OF PYRAZINOPORPHYRAZINE NETWORK POLYMER-SUPPORTED METAL (II)-BASED CATALYSTS

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**Abstract** Chloranil through condensation reaction with vicinal diamine such as diaminomaleonitrile produced heterocyclic monomer, *p*-benzoquinonebis[2,3-*b*; 2',3'-*b'*]pyrazine-5,6-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'*]pyrazinoporphyrazine]-based network polymer (2H-Pz). The tetranitril monomer was cyclo-tetramerised using metal salt and quinoline affording the corresponding 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 proved to be of high molecular masses which confirm the efficiency of tetramerization polymerization and complexation reactions. The prepared pyrazinoporphyrazines were used as efficient catalysts for the oxidation of thiophenol and benzylthiol to their disulfides in the presence of air atmosphere. The results of oxidation of thiophenol and benzylthiol show that after 15 min the maximum yield of the corresponding disulfides reached 95%, 91%, respectively.

**Keywords:** Pyrazinoporphyrazine; Polymer-supported metal (II)-based catalysts; Chloranil.

### INTRODUCTION

Tetrapyrazinoporphyrazine is one of the phthalocyanine derivatives having two nitrogen atoms at equivalent 1,4-positions of the phthalocyanine benzene units. Due to the additional nitrogen atoms, tetrapyrazinoporphyrazines are less electron-rich than the corresponding phthalocyanine<sup>[1]</sup>. Macroheterocycle systems such as porphyrins, tetrabenzoporphyrazines and their aza analogues are interesting objects of extensive studies and practical applications, science, industry and medicine. Porphyrazine complexes of zinc, aluminium and other metals show anticancer properties and uses in photodynamic therapy<sup>[2]</sup>. Base-induced cyclotetramerisation of the aromatic dinitriles with magnesium butoxide in refluxing butanol generates the peripherally peralkynylated phthalocyanine or naphthalocyanine analogues, namely the tetrapyrazinoporphyrazines and tetra-6,7-quinoxalinoporphyrazines, respectively<sup>[3]</sup>. The pyrazinoporphyrazine system (metal-free, 2H-PyzPz, zinc and copper derivatives) has been synthesized by tetramerization of 2,3-dicyanopyrazine monomer unit<sup>[4]</sup>. 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<sup>[5]</sup>. Nitrogen

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substituted porphyrazines, the second type of heteroatom-derivatized macrocycle, were reported and prepared from the readily derivatized diaminomaleonitrile (DAMN)<sup>[6]</sup>. Chloranil through condensation reaction with 4-amino-3-methyl-1-phenyl-5-(hydroxyl, mercapto or imino)-pyrazole produced new cyanine dyes<sup>[7]</sup>.

In recent years, there has been a growing emphasis on using organic components for the construction of microporous materials. It is clear that by careful selection of organic precursors it will be possible to exert precise control over the chemical nature of the accessible surface and to introduce specific molecular recognition or catalytic sites, thus facilitating chemoselective adsorption and the design of highly efficient heterogeneous catalysts. Soluble linear polymer ligands provide the basis for the best catalysts, whereas insoluble resins lead to diffusional problems. In this form cobalt (II) phthalocyanines have proved very useful for catalyzing the autoxidation of thiols<sup>[8–10]</sup>. These reactions require the presence of a base, and free amino groups on the polymer backbone serve admirably in this respect. Industrially, disulfides have wide applications as vulcanizing agents for rubbers and elastomers, giving them excellent tensile strength. More recently an organic quinone polymer containing sulphonic acid groups has been used to support palladium (II), yielding a catalyst effective for the conversion of ethylene to acetaldehyde<sup>[11]</sup>. New fully conjugated 2H- and metal-pyrazinoporphyrazines and 2H- and metal-phthalocyanine network polymers and their conductivity were reported<sup>[12, 13]</sup>. The aim of this work is the synthesis of new pyrazinoporphyrazine-based network polymers containing quinone moiety to be useful as supported metal (II)-based catalysts.

## EXPERIMENTAL

### Characterization

Fourier-transform infrared spectrometer (8101 M-Shimadzu) was used in spectral measurements. UV-Vis spectra were obtained using a Unicam UV-Vis spectrometer. NMR spectra were recorded in deuteriochloroform, on a Varian VXR 400S NMR spectrometer operating at 400 MHz (<sup>1</sup>H-NMR) and 100 MHz (<sup>13</sup>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. Molecular masses (number average  $M_n$ , weight average  $M_w$ ) were determined by gel permeation chromatography, GPC, (Polymer Laboratories, PL-GPC 20) using polystyrene standards and dilute polymer solutions (10 mg/5 mL) in tetrahydrofuran (THF) at room temperature with the rate of 1 mL/min. Elemental analysis was performed with a 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*-Benzoquinone Bis[2,3-*b*; 2',3'-*b'*]pyrazine-5,6-dinitrile (**3**)

A mixture of unimolar ratio of *p*-chloranil **1** (0.01 mol) and bimolar ratio of diaminomaleonitrile **2** (0.02 mol) was refluxed in ethanol (50 mL) containing pyridine (20 mL) for 6 h. The reaction mixture changed to deep 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. IR (KBr):  $\nu$  (cm<sup>-1</sup>), 1615 (C=C), 1685 (C=O), 2228 (CN), 3354 (NH); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  = 2.85 (s, H, NH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  = 100.4, 115.5, 135.7, 180.4. Anal. calcd. for C<sub>14</sub>H<sub>4</sub>N<sub>8</sub>O<sub>2</sub> (MWt: 316.05) requires C, 53.17; H, 1.27; N, 35.43 %. Found: C, 53.37; H, 1.44; N, 35.55 %.

### Synthesis of tetra *p*-Benzoquinonebis[2,3-*b*; 2',3'-*b'*]pyrazinoporphyrazine]-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 (2 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<sup>-1</sup>), 1514 (C=N), 1618 (C=C), 1692 (C=O). 3347, 3363 (NH) UV-Vis  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm: 345, 418, 695. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  = 0.07, 1.38 (s, NH). Anal. calcd. for the expected polymer repeat unit C<sub>32</sub>H<sub>14</sub>N<sub>12</sub>O<sub>4</sub> (MWt = 634.6) requires C, 60.51; H, 2.20; N, 26.47 %. Found: C, 60.64; H, 2.33; N, 26.55%.

**Synthesis of tetra *p*-Benzoquinonebis[2,3-*b*; 2',3'-*b'*]pyrazinoporphyrazinato-metal II-based Network Polymers (M-Pz) (4b–4d)**

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 (2 mL) at 200°C 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 column chromatography (eluent: dichloromethane). The polymer was vacuum dried overnight.

**4b:** IR (KBr):  $\nu$  (cm<sup>-1</sup>), 1506 (C=N), 1605 (C=C), 1688 (C=O), 3349 (NH). UV-Vis  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm): 350, 410 (shoulder), 610, 695. Anal. calcd. for the expected polymer repeat C<sub>32</sub>H<sub>12</sub>N<sub>12</sub>O<sub>4</sub>Co (MWt = 687.5) requires C, 55.85; H, 1.74; N, 24.43; Co, 8.57%. Found: C, 55.96; H, 1.82; N, 24.55; Co, 8.63%.

**4c:** IR (KBr):  $\nu$  (cm<sup>-1</sup>), 1508 (C=N), 1607 (C=C), 1690 (C=O), 3345 (NH). UV-Vis  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm): 365, 420 (shoulder), 615, 705. Anal. calcd. for the expected polymer repeat C<sub>32</sub>H<sub>12</sub>N<sub>12</sub>O<sub>4</sub>Ni (MWt = 687.27) requires C, 55.87; H, 1.74; N, 24.44; Ni, 8.54%. Found: C, 55.98; H, 1.82; N, 24.49; Ni, 8.58%.

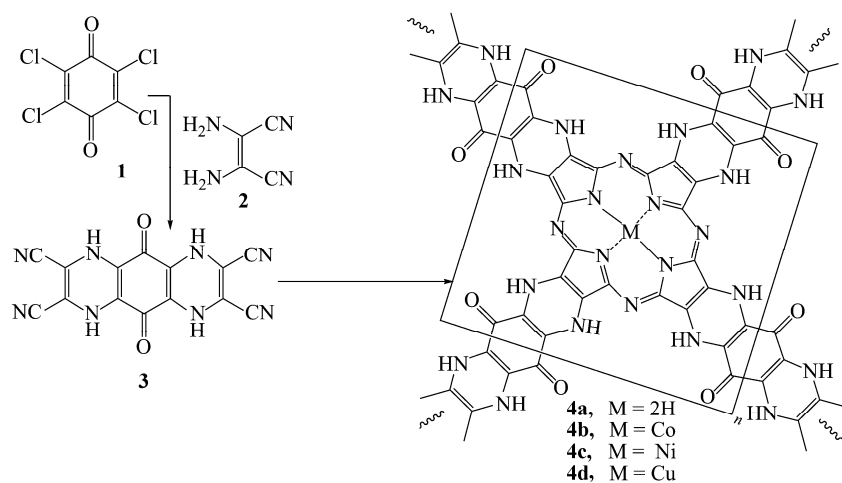
**4d:** IR (KBr):  $\nu$  (cm<sup>-1</sup>), 1505 (C=N), 1604 (C=C), 1694 (C=O), 3352 (NH). UV-Vis  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm): 350, 412 (shoulder), 634, 700. Anal. calcd. for the expected polymer repeat C<sub>32</sub>H<sub>12</sub>N<sub>12</sub>O<sub>4</sub>Cu (MWt = 692.13) requires C, 55.48; H, 1.73; N, 24.27; Cu, 9.18%. Found: C, 55.59; H, 1.76; N, 24.32; Cu, 9.23%.

**Oxidation of Thiols (Catalytic Process): General Procedure**

A round bottom flask was charged with thiol derivative (10 mmol), acetonitrile (30 mL) and metal free- or metal-Pz catalyst (1 g). The resulting mixture was stirred under reflux condition for 15 min. The progress of reaction was monitored by TLC (chloroform was used as solvent for TLC). After completion of the reaction, a solution of 1% aqueous sodium thiosulfate (30 mL) was added and the mixture was stirred for 10 min. The mixture was diluted with chloroform and the catalyst was removed by simple filtration. The residue was chromatographed on a short column of silica gel using n-hexane as eluent. Dithiol product was obtained in good yield. The pure diphenyl disulfide was obtained as colourless crystals with average yield for all catalysts 95%, Mp. 59°C (Ref. [24], 60°C); IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3055, 1567, 1478, 1432, 732, 692, 455. The pure dibenzylidysulphide was obtained as colourless solid with average yield for all catalysts 91%, Mp. 68°C (Ref. [18], 67°C).

**RESULTS AND DISCUSSION**

Chloranil through condensation reaction with vicinal diamine such as diaminomaleonitrile produced heterocyclic monomer, *p*-benzoquinonebis[2,3-*b*; 2',3'-*b'*]pyrazine-5,6-dinitrile **3**. The tetranitrile monomer **3** was cyclo-tetramerised using lithium/pentanol and acetic acid affording the corresponding tetra *p*-benzoquinone bis[2,3-*b*; 2',3'-*b'*]pyrazinoporphyrazine)-based network polymer (2H-Pz) **4a**. The tetranitril monomer was cyclo-tetramerised using metal salt and quinoline affording the corresponding porphyrazinato-metal II-based network polymers (M-Pz), **4b–4d**, 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 proved to be of high molecular masses which confirm the efficiency of tetramerization polymerization and complexation reactions. The prepared porphyrazines display good solubility in organic solvents, such as THF, diethyl ether, ethyl acetate, acetone, dichloromethane, chloroform and dimethylsulfoxide.



**Scheme 1** 2H- and metal pyrazinoporphyrazines derived from tetranitrile

### Infrared and UV-Vis Spectra

IR spectral data of precursor **3** show intense bands at 1607, 1689, 2234 and 3338  $\text{cm}^{-1}$  assigned to C=C, C=O, C $\equiv$ N and NH groups, respectively (Fig. 1). IR spectrum of metal free pyrazinoporphyrazine-based network polymer 2H-Pz **4a** shows a broad band at 1517  $\text{cm}^{-1}$ , which is assignable to the stretching vibration of the C=N bond. The absorption values of the C=N vibration at 1509, 1512, and 1507  $\text{cm}^{-1}$  (see experimental) for Co-Pz **4b**, Ni-Pz **4c** and Cu-Pz **4d** respectively, are lower by about 3–10  $\text{cm}^{-1}$  than those for the metal free 2H-Pz **4a**, which indicates the coordination of azomethine nitrogen atom to metal ions in the complexes. Moreover, there is an extra broad band at 3354  $\text{cm}^{-1}$ , assignable to the stretching vibration of the N–H bond in free metal pyrazinoporphyrazine complex 2H-Pz **4a**. This stretching vibration of the N–H bond does not appear in the spectra of metal complexes **4b–4d** which means that the NH group is involved in metal-ligand formation. UV-Vis spectrum of 2H-Pz **4a** in dichloromethane solution shows a strong band at 345 nm (Fig. 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 618 and 695 nm. These bands are in good agreement with the absorption spectra reported in the literature<sup>[14]</sup>. The electronic absorption spectra of the metal complexes **4b–4d** in dichloromethane solution are presented in Fig. 2. Two transitions are dominated at higher-energy B-band (broad bands around 357 nm and shoulder bands around 415 nm) which can be assigned to the  $\pi$ - $\pi^*$  and/or d- $\pi^*$  transitions in the fused pyrolopyrazine ring structure<sup>[15, 16]</sup>. Two characteristic well developed intense lower-energy, Q-bands, (around 615 nm and 700 nm) are observed. The shoulder band is usually attributed to the 1s  $\rightarrow$  4d transition<sup>[17]</sup>. It was demonstrated already in

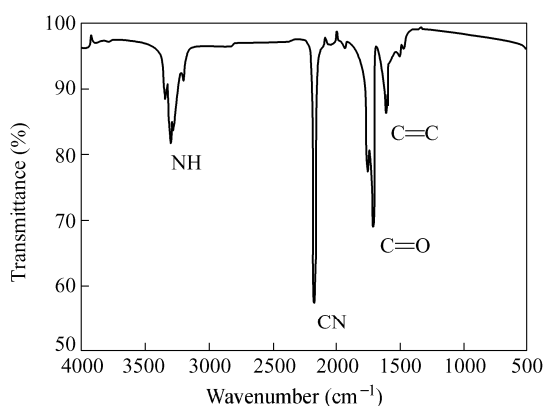


**Fig. 1** FT-IR spectrum of tetranitrile monomer **3**

early theoretical work<sup>[18, 19]</sup>, 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 410–420 nm below the Q-band excitation for all of the M-Pz 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 pyrazinoporphyrazines (Fig. 2). It has been suggested that both Q and B bands can be influenced by the metal-to-ligand charge-transfer bands<sup>[20]</sup>. It is clear that the absorption bands for metal complexes extend beyond 800 nm. Thus, these pyrazinoporphyrazines could be useful in the field of optical data storage and for security printing which require absorbance in the near infrared region.

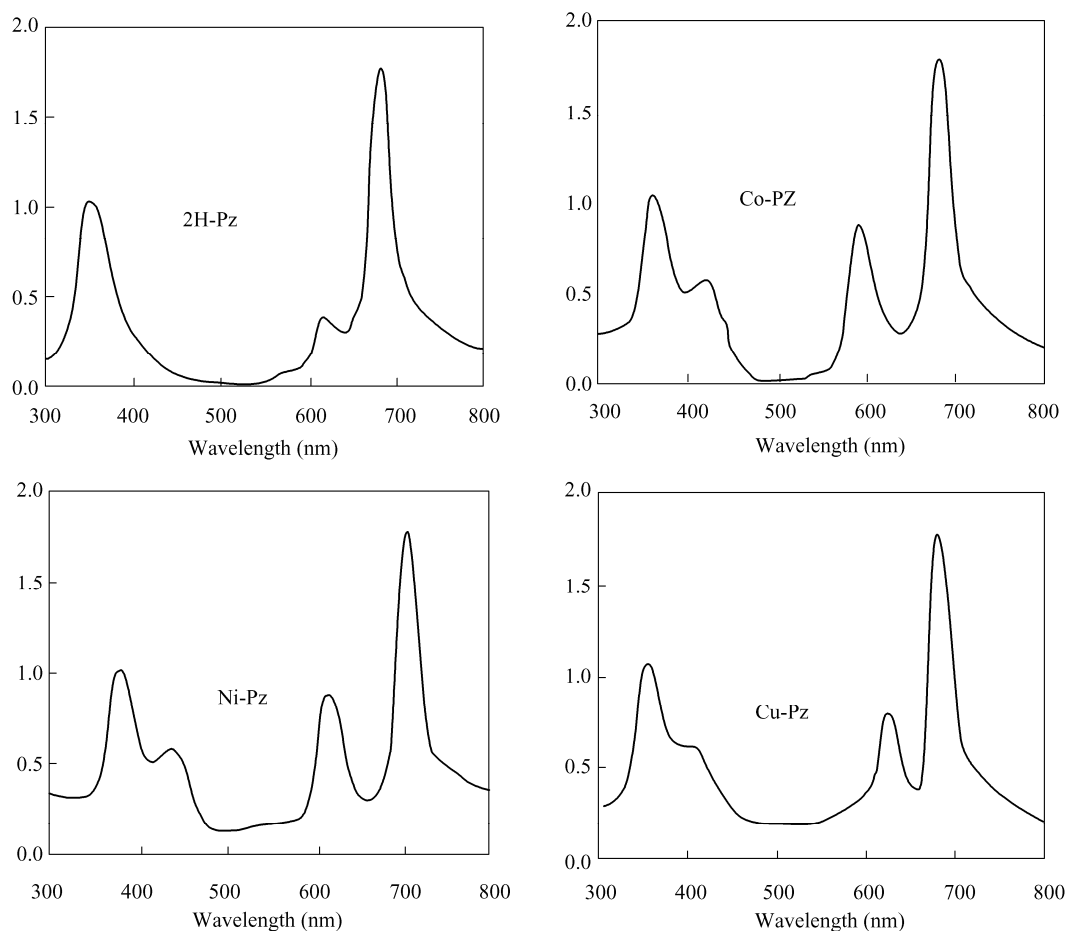


**Fig. 2** UV-Vis spectra of metal free- and metal-pyrazinoporphyrazine network polymers **4a–4d**

#### **<sup>1</sup>H-NMR and Molecular Mass Measurements of the Prepared Network Polymers**

In accordance with the structure of *p*-benzoquinonebis[2,3-*b*; 2',3'-*b'*]pyrazine-5,6-dinitrile **3**, the <sup>1</sup>H-NMR spectrum revealed a singlet at  $\delta = 2.85$  assignable to NH proton (Fig. 3). Elemental analytical results and <sup>13</sup>C-NMR spectral data of the new tetranitrile **3** are consistent with the assigned formulation (see Experimental, Scheme 1 and Fig. 4). <sup>1</sup>H-NMR spectrum of free metal pyrazinoporphyrazine)-based network polymer 2H-Pz **4a** reveals two signals at  $\delta = 0.07$  and 1.38 assignable to NH protons (Fig. 5). The presence of two signals around  $\delta = 1$  assignable to NH protons (deshielded by macrocyclic structure) in <sup>1</sup>H-NMR spectrum of 2H-Pz **4a** gives direct evidence of the formation of an unsymmetrical tetradentate ligand. Elemental analyses for 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 those calculated for the expected polymer repeat unit. Moreover, metal content and high molecular masses of the synthesized polymers confirm the efficiency of tetramerization polymerization and complexation reactions. The narrow molecular weight distribution (Table 1) in all samples, with  $M_w/M_n = 2.75$ –3.04, implies that the polymerization follows a single-site reaction mechanism. High molar mass and good solubility of these polymers allow conventional solution-based polymer processing techniques.

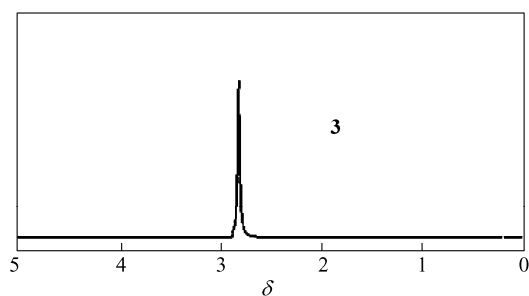


**Fig. 3**  $^1\text{H}$ -NMR spectrum of tetranitrile monomer **3** in  $\text{CDCl}_3$

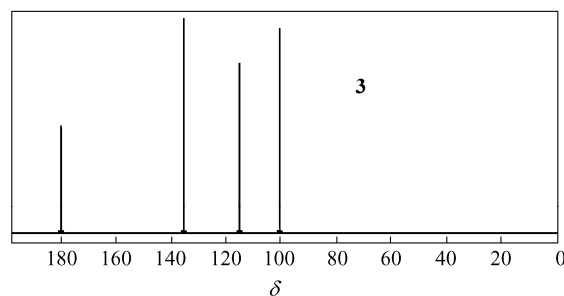


**Fig. 4**  $^{13}\text{C}$ -NMR spectrum of tetranitrile monomer **3** in  $\text{CDCl}_3$

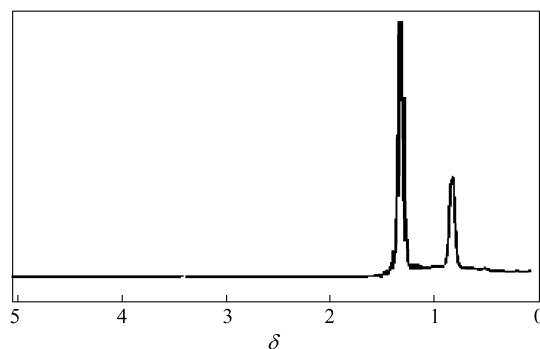


**Fig. 5**  $^1\text{H}$ -NMR spectrum of 2H-Pz polymer **4a** in  $\text{CDCl}_3$

**Table 1.** Characteristic data of the prepared pyrazinoporphyrazine network polymers

| No.       | Sample | Yield (%) | $M_p$ ( $^{\circ}\text{C}$ ) | $M_n$ | $M_w$  | Polydispersity ( $M_w/M_n$ ) | BET area ( $\text{m}^2/\text{g}$ ) |
|-----------|--------|-----------|------------------------------|-------|--------|------------------------------|------------------------------------|
| <b>4a</b> | 2H-Pz  | 83        | 222–224                      | 44436 | 122312 | 2.75                         | 466                                |
| <b>4b</b> | Co-Pz  | 77        | 213–215                      | 41618 | 120646 | 2.89                         | 430                                |
| <b>4c</b> | Ni-Pz  | 85        | 193–195                      | 39414 | 119866 | 3.04                         | 455                                |
| <b>4d</b> | Cu-Pz  | 81        | 207–209                      | 43647 | 121947 | 2.79                         | 442                                |

### Thermal Analysis

Thermal stability of the copolymers was also examined. TGA thermograms of the synthesized pyrazinoporphyrazines are shown in Fig. 6. The results show that metal-free pyrazinoporphyrazine network polymer **4a** has significantly comparable degradation temperature ( $T_d$ ) at  $410^{\circ}\text{C}$ . However, metal-pyrazinoporphyrazine network polymers **4b–4d** show better thermal stability with a main degradation step taking place at  $428^{\circ}\text{C}$  for Co-Pz,  $430^{\circ}\text{C}$  for Ni-Pz and  $442^{\circ}\text{C}$  for Cu-Pz.

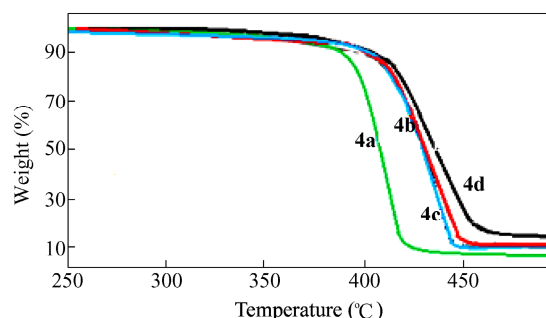
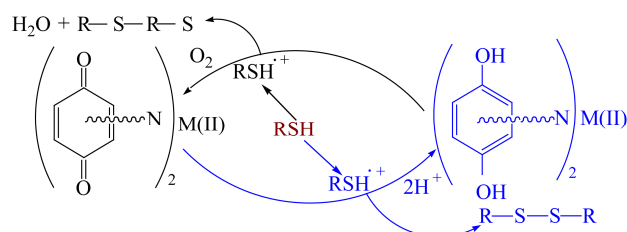


**Fig. 6** TGA of metal free- and metal-pyrazinoporphyrazine network polymers **4a–4d** with a heating rate of 10 K/min

### Catalytic Activity of the Prepared Polymers

The prepared pyrazinoporphyrazines **4a–4d**, were used as efficient catalysts for the oxidation of benzyl and aromatic thiols to their disulfides in the presence of air atmosphere. BET surface areas of the prepared catalysts are shown in Table 1. Nitrogen adsorption measurements show that the materials have high surface areas in the range 430–466 m<sup>2</sup>g<sup>−1</sup> with very significant adsorption at low relative pressure ( $P/P_0 < 0.02$ ) indicating microporosity<sup>[21]</sup>. Small differences have been observed in the metal-Pz BET surface areas. The results of oxidation of thiophenol and benzylthiol show that after 15 min the maximum yield of the corresponding disulfides reached 95% and 91%, respectively (see Experimental). Thus, metal-pyrazinoporphyrazines are far more effective catalysts of the oxidation of thiols indicating the influence of the presence of pyrazine ring on the promotion of the catalytic process<sup>[22, 23]</sup>. As expected, quinone rings along the backbone of the polymer were found to be effective in the pathway of catalytic reaction<sup>[11]</sup>. Spectral analysis of the used catalyst after the completion of the reaction showed that the catalyst containing quinone rings was transformed to catalyst containing quinol rings as a result of oxidation of thiols (Scheme 2). IR spectra of the used catalyst showed disappearance of the band assignable for (C=O) group and the presence of broad band at 1654 and 3395 cm<sup>−1</sup> assignable to phenolic group indicating oxidation process. Also, <sup>1</sup>H-NMR (CDCl<sub>3</sub>) of the used catalyst shows multiple band at 7.74–7.96 and broad singlet band at 11.56 assignable for phenyl rings and (OH) groups, respectively. The mechanism of the oxidation of phenols is extremely complex and is not yet fully understood. It is generally accepted that the oxidation of phenol by molecular oxygen is basically an electrophillic reaction and the rate limiting step is the reaction between the aryloxy radical with oxygen<sup>[24, 25]</sup>. At elevated temperatures and in the presence of water and catalyst, oxygen is capable of different oxidation reactions, *i.e.* it can substitute an oxygen atom into an aromatic ring to form a dihydric phenol or quinone. Rollmn<sup>[26]</sup> produced a bifunctional polymeric catalyst which contained both Co(II) tetraphenylporphyrin and a base to act as a proton acceptor. This system readily catalysed the oxidation of thiols by molecular oxygen. Characterization and activity of copper and nickel catalysts for the oxidation of phenol aqueous solutions were reported<sup>[27]</sup>. Reusability of the quinolic catalyst, the phenolic groups can be auto oxidized in the presence of air oxygen<sup>[28]</sup>, was subjected to a second run of the oxidation process with the same substrate giving converged yields of disulfides and catalyst with quinone structure. We have thus found that the prepared catalysts **4a–4d** can be reused several times. A representative reaction sequence is shown in Scheme 2. Yield percentage (Table 2) of disulphides obtained by oxidation catalytic process shows that metal pyrazinoporphyrazine catalysts indicate higher catalytic activity in comparison with metal free pyrazinoporphyrazine catalyst. The activity of the complexes is affected not only by the nature of the complex-forming metal but also by the BET area values of the catalysts. The pure diphenyldisulfide and dibenzylidisulphide were obtained with average yield for all catalysts around 95% and 91%, respectively.



**Scheme 2** A representative reaction sequence for the oxidative catalytic activity of the prepared polymers

**Table 2.** Yield percentage of disulphides obtained by oxidation catalytic process

| No.       | Catalyst | Diphenyldisulphide yield (%) | Dibenzyliddisulphide yield (%) |
|-----------|----------|------------------------------|--------------------------------|
| <b>4a</b> | 2H-Pz    | 89                           | 87                             |
| <b>4b</b> | Co-Pz    | 98                           | 95                             |
| <b>4c</b> | Ni-Pz    | 95                           | 91                             |
| <b>4d</b> | Cu-Pz    | 93                           | 90                             |

## CONCLUSIONS

Chloranil through condensation reaction with vicinal diamine such as diaminomaleonitrile produced heterocyclic tetranitrile monomer which was found to be useful in generation of new metal free and metal pyrazinoporphyrazine network-polymer support metal (II)-based catalysts. The prepared pyrazinoporphyrazines were used as efficient catalysts for the oxidation of thiophenol and benzythiol to their disulfides in the presence of air atmosphere.

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