NOVAS TETRA (1,4-DITIIN)PORFIRAZINAS E SUAS APLICAÇÕES COMO FOTOCATALISADORES PARA PURIFICAÇÃO DE ÁGUAS: UMA ABORDAGEM PARA QUÍMICA VERDE

NEW TETRA (1,4-DITHIN)PORPHYRAZINES AND THEIR APPLICATION AS PHOTOCATALYSTS FOR PURIFYING ENVIRONMENTAL WATERS: AN APPROACH TO GREEN CHEMISTRY

مركبات 1 و 4 (داى ثاين) بورفيرازين جديدة وتطبيقاتها كحفازات ضوئية لتنقية المياه فى البيئة: كيمياء صديقة للبيئة

H. H. Abdel-Razik^{*1,2}, H. A. Almahy^{1,3}, Y. A. El-Badry^{1,4}

¹Chemistry Department, Faculty of Science, Taif University, SAUDI ARABIA

²Chemistry Department, Faculty of Science, Damietta University, New Damietta, EGYPT

³Chemistry Department, Faculty of Science, Bihari University, Khartoum, SUDAN

⁴Chemistry Department, Faculty of Specific Education, Ain Shams University, Cairo, Egypt.

** Corresponding author*

e-mail: hamada@du.edu.eg

Received 25 February 2018; received in revised form 01, 12, 14 March 2018; accepted 15 March 2018

RESUMO

2,3-dicloro-5,6-dimetilbenzoquinona reagiu com di(sodio-tio)maleonitrila para produzir a tianona heterocíclica, 6,7-dimetil-5,8-dioxo-5,8-diidro-1,4-benzoditiina-2,3-dicarbonitrila foi ciclo-tetramerizado na presença de lítio/pentanol e ácido acético produzindo tetra 6,7-dimetil-5,8-dioxo-5,8-diidro-1,4-benzoditiina-porfirazina (2H-Pz). Do mesmo modo, o composto dicarbonitril foi ciclo-tetramerizado utilizando o sal metálico e quinolina para formar 6,7-dimetil-5,8-dioxo-5,8-diidro-1,4-benzoditiina-porfirazinato metálico II (M-Pz), onde M é Co, Ni ou Zn). A investigação básica, dados espectrais de Infravermelho e RMN dos compostos preparados estão de acordo com as estruturas propostas. A fotoatividade das porfirazinas sintetizadas foi alcançada para a faixa de luz óbvia. As porfirazinas preparadas apresentaram catalisadores sensibilizados eficientes através da utilização da radiação solar para a total foto oxidação fotocatalítica de tiofenol e benziltiol nos seus dissulfetos (com um rendimento médio de 93% e 90%, respectivamente) na presença de ar atmosferico em 20 minutos.

Palavras-chave: Tetra(1,4-ditiin)Porfirazinas, Cicloestruturação, Atividade de oxidação fotocatalítica

ABSTRACT

2,3-Dichloro-5,6-dimethylbenzoquinone reacted with di(sodiothio)maleonitrile to produce heterocyclic thianone, 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-2,3-dicarbonitrile which was cyclo-tetramerized in the presence of lithium/pentanol and acetic acid producing tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrzine (2H-Pz). Likewise, the dicarbonitrile compound was cyclo-tetramerized in the presence of metal salt and quinoline affording tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrzinato-metal II (M-Pz), M is Co, Ni or Zn. Photoactivity of the synthesized porphyrzines was reached out to the visible light range. The prepared porphyrzines showed efficient sensitized catalysts by using of solar energy for the completely photocatalytic oxidation of thiophenol and benzyl thiol to their disulfides (with an average yield of 93% and 90%, respectively) in the presence of air atmosphere within 20 minutes.

تفاعل 2و3-داي كلورو-5و6-داي ميثيل بنزوكينون مع داي (صوديويثيو) ماليونيتريل لانتاج حلقة ثيانون غير متجانسة من 6و7-داميثيل-5و8-داي أكسو-5و8-داي هيدرو-1و4-بنزو داي ثاين-2و3-داي كربونيتريل الذي تم تحويله في وجود ليثيوم/بنتانول وحمض الخليكمنتجا رباعي 6و7-داميثيل-5و8-داي أكسو-5و8-داي هيدرو-1و4-بنزو داي ثاين بورفيرازين وكذلك تم تحويل المركب داي كربونيتريل بواسطة ملح معدني وكينولين منتجا رباعي 6و7-داي ميثيل-5و8-داي أكسو-5و8-داي هيدرو-1و4-بنزو داي ثاين بورفيرازيناتو- M(II) و M هي كوبلت أو نيكل أو زنك. النشاط الضوئي للبورفيرازينات المحصورة امتد لمنطقة الضوء المرئي. البورفيرازينات المحصورة أظهرت كفاءة في حفز الأكسدة في ضوء الشمس للثيوفينول والبنزيل ثيول لتكوين مشتقاتهما من الداي سلفايد بمتوسط انتاج 93% , 90% على التوالي في 20 دقيقة.

الكلمات المفتاحية: رباعي (1و4-داي ثاين) بورفيرازين , تحويل رباعي , الأكسدة بالحفز الضوئي

INTRODUCTION

Metal and free metal-tetra (1,4-dithin)porphyrazines which have the extended delocalized 18π -electrons of conjugated macrocyclic molecules have good photocatalytic properties in oxidation and degradation process of environmental organic pollutants. Solar light and oxygen in air can be used using porphyrazine photocatalysts to degrade organic pollutants in water which become promising research area at present and is a new concept of green chemistry.

Metallic-porphyrazine derivatives having 2-methyl-2-pentenyl moiety fused to each pyrrole ring were synthesized starting with unsaturated dicarbonitrile derivative¹.

Iron (II)-Tetra (1,4-dithin)porphyrazine derivative is an efficient catalyst capable to activate molecular oxygen for degradation of organic compounds without light excitation². In our previous work, dielectric properties of fully conjugated 2H- and metal-pyrazinoporphyrazine macromolecules were investigated³.

The photocatalytic oxidative debasement of natural poison with atomic oxygen enacted by a novel biomimetic impetus $ZnPz(dtn-COOH)_4$ was studied⁴. Zinc(II)-tetracarboxyl-tetra(1,4-dithin)porphyrazine was prepared and its photocatalytic activity as a catalyst for activation of molecular oxygen under visible light to make degradation of rhodamine B dye in aqueous solution⁵.

Tetra (1,4-dithin) metal-free (H_2Pz) and metallo-porphyrazines derived from 2,3-dicyano-5-propylbromine-1,4-dithin, were synthesized and showed a good photocatalytic activity⁶. The precursor 2,3-dithiolate-1,4-dithin was prepared

from di(sodiothio)maleonitrile and 1,2-dibromoethane, and the other precursor 4-pentyloxy-phthalic nitrile was synthesized from n-amyl alcohol and 4-nitrophthalonitrile. These precursors were subjected to afford tri(pentyloxy)phenyl(1,4-dithin)porphyrazines⁷.

Synthesis, characterization and spectroscopic studies of pyrazino-porphyrazine polymer-supported metal (II)-based catalysts were investigated⁸. Dependence on the expected photocatalytic properties of porphyrazine compounds, this research focuses on the preparation, characterization, spectral investigation and photocatalytic activity of metal free and Metal-tetra (1,4dithin)porphyrazines and their applications as a green oxidation catalyst for purifying environmental waters.

MATERIALS AND METHODS

All chemicals and solvents used in this research were of reagent grade. Di(sodiothio)maleonitrile was purchased from Synthon-Chemicals GmbH & Co. KG, Germany. 2,3-Dichloro-5,6-dimethylbenzoquinone, lithium, pentanol, quinoline, thiophenol, and benzyl thiol were purchased from Sigma Aldrich. Cobalt chloride, nickel II chloride and zinc chloride were purchased from Fairsky Industrial Co., Limited.

Characterization

FTIR spectrophotometer (8101 M Shimadzu) and UV-Vis (Systronics 168) spectrophotometer were used in spectral data measurements. Varian VXR 400S NMR spectrometer operating at 400 MHz (1H NMR) and 100 MHz (^{13}C NMR) was used for getting

nuclear magnetic resonance spectral information in deuterio-chloroform with tetramethylsilane as internal standards. Metal content data measurements were carried out using atomic absorption spectrometer (Perkin Elmer Analyst 300, AAS). Structure analyses were measured using spectrometer (PerkinElmer 2400 CHN).

BET surface areas were computed from the nitrogen adsorption isotherms at 77 K by utilizing a Micrometrics ASAP2000 surface analyzer. Photo-reactor made of glass with a cube body was used for the oxidation reaction. Halogen lamp (300 W) outfitted with a cut off filter at 400 nm was utilized as the illumination source was subjected to light the reactants. Photocatalytic reactor worked in a batch mode with continuous stirring. The body of the reactor was surrounded by a reflector such as polished aluminum thin layers. Air was pushed to the solution (to be supplied by dissolved oxygen) at constant flow rate using a micro-air compressor.

Preparation of 6,7-Dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithine-2,3-dicarbonitrile **3**

A mixture of 2,3-Dichloro-5,6-dimethylbenzoquinone **1** (0.02 mol) and di(sodiothio)-maleonitrile **2** (0.02 mol) was heated in dimethylformamide (75 mL) at 85 °C for 10 h. The reaction mixture becomes brown at the end of the reaction. The reaction mixture was sifted while hot, precipitated by ice water. The yield was collected, washed with hot water, dried and recrystallized from ethanol. 88% yield (yellowish crystals). Molecular Formula: $C_{12}H_6N_2O_2S_2$, Formula Weight: 274.318, Calculated: C (52.54%) H (2.20%) N (10.21%), Found: C (52.77%), H (2.31%), N (10.36%).

Preparation of Tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrazine (2H-Pz) **4a**

A mixture of **3** (137.159 mg, 0.5 mmol) in pentanol (20 mL) and Lithium metal (20 mg, 2.8 mmol) was refluxed for 12 h. Subsequent to cooling, acetic acid (0.2 mL) was added to the reaction mixture and the product was collected by filtration. Purification of the pale green product was carried out by column chromatography (eluent: dichloromethane) and precipitated from

methanol. The precipitate was vacuum dried. Analytical calculated for **4a**: Molecular Formula: $C_{48}H_{26}N_8O_8S_8$, Formula Weight: 1099.288, Calculated: C (52.44%) H (2.38%) N (10.19%), found C (52.58%) H (2.49%) N (10.31%).

Preparation of Tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrazinato-metal II (M-Pz) **4b-4d**

Dicarbonitrile compound **3** (137.159 mg, 0.5 mmol) was subjected to yield the corresponding porphyrazines on heating with 0.75 mmol of metal salt (cobalt chloride, nickel II chloride or zinc chloride) in quinoline (50 mL) at 200 °C for 12 h. The yield was dissolved in acetone, so the un-caught metal was precipitated and expelled from the solution by filtration. The abundance of methanol was added to the product solution precipitating green (**4b**, **4c**) or dark green (**4d**) solids which were separated and purified by column chromatography on silica gel (eluent: dichloromethane).

The product was precipitated from methanol and vacuum dried. Analytical calculated for **4b**: Molecular Formula: $C_{48}H_{24}CoN_8O_8S_8$, Formula Weight: 1156.206, Calculated: C (49.86%) H (2.09%) Co (5.10%) N (9.69%), found C (49.99%) H (2.17%) Co (5.22%) N (9.81%); for **4c**: Molecular Formula: $C_{48}H_{24}NiN_8O_8S_8$, Formula Weight: 1155.966, Calculated: C (49.87%) H (2.09%) N (9.69%) Ni (5.08%), found C (49.98%) H (2.19%) N (9.82%) Ni (5.17%); for **4d**: Molecular Formula: $C_{48}H_{24}ZnN_8O_8S_8$, Formula Weight: 1162.681, Calculated: C (49.58%) H (2.08%) N (9.64%) Zn (5.63%), found C (49.71%) H (2.20%) Zn (5.78%) N (9.82%).

Oxidation of Thiols (Catalytic Process)

A round bottom flask was charged with thiophenol or benzyl thiol (10 mmol), acetonitrile (30 mL) and metal free- or metal-Pz catalyst (1 g). The subsequent blend was stirred at room temperature and was subjected to visible-light irradiation of the sensitizers using a halogen lamp (300 W) furnished with a cutoff filter at 400 nm. The advance of the reaction was checked by TLC (chloroform was utilized as dissolvable for TLC).

After fulfillment of the reaction, a solution of 1% aqueous sodium thiosulfate (30 mL) was added and the reaction mixture was stirred for 10 minutes. The mixture was diluted with chloroform

and the catalyst was removed by basic filtration. The precipitate was chromatographed on a short column of silica gel using chloroform as eluent. The pure diphenyl disulfide was created as colorless crystals (melting point 59 °C)⁹ with an average yield 93% for all (1,4-dithin)porphyrzine catalysts. The pure dibenzyl disulfide was obtained as colorless solid (melting point 68 °C)¹⁰ with an average yield for all catalysts 90%.

RESULTS AND DISCUSSION

2,3-Dichloro-5,6-dimethylbenzoquinone **1** reacted with di(sodiothio)-maleonitrile **2** affording heterocyclic compound (thianone), 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithine-2,3-dicarbonitrile **3**. Cyclotetra-merization of dicarbonitrile compound **3** was carried out using lithium/pentanol and acetic acid producing tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrzine (2H-Pz) **4a**. Dicarbonitrile compound **3** was cyclotetramerized in the presence of metal salt and quinoline producing tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodi-thin-porphyrzinato-metal II (M-Pz), M = Co **4b**, Ni **4c** or Zn **4d**.

Elemental analytical data, infra-red and nuclear magnetic resonance spectral data of the synthesized products are in agreement with their chemical structures. Molecular masses and metal contents of the prepared compounds assure the efficiency of cyclotetramerization and complexation reaction processes.

Infrared and ultra violet-visible spectrum

IR spectral data of product **3** demonstrates intense bands at 1602, 1667 and 2224 cm⁻¹ related to C=C, C=O, and CN groups, respectively (table1). IR spectrum of metal-free [1,4]dithinporphyrzine 2H-Pz **4a** shows an expansive band at 1522 cm⁻¹, which is assignable to the stretching vibration of the double bond of C=N. Absorption values are shown for C=N double bond vibration at 1508, 1514, and 1512 cm⁻¹ for Co-Pz **4b**, Ni-Pz **4c**, and Zn-Pz **4d**, respectively, are lower by around 8-14 cm⁻¹ than those for the metal-free 2H-Pz **4a**, indicating the coordination of azomethine nitrogen atom to the metal in the porphyrzine complexes.

Also, there is an additional band at 3335 cm⁻¹, assigned to the stretching vibration of the N-H bond in free metal (1,4-dithin)porphyrzine 2H-

Pz **4a**. This stretching vibration of the N-H bond does not appear in the spectra of metal complexes **4b-4d** which assure that NH group is used in metal-ligand formation. UV-Vis spectrum of 2H-Pz **4a** in chloroform solution shows a sort band at 342 nm (Table 1).

The Q bands related to the difference between the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy level, that is, the π - π^* transitions in 2H-Pz **4a** are seen at 637, 708 nm. These bands are in concurrence with the retention spectra mentioned in literature¹¹. The electronic absorption spectra of the metal complexes **4b-4d** in chloroform solution demonstrate two transitions commanded at higher-energy B-band (wide bands around 325 nm and shoulder bands around 423 nm) which can be related to the π - π^* and/or d- π^* transitions in the combined pyrrolo (1,4-dithin) ring moiety^{12,13}.

Two lower energy, Q-bands, (around 645 nm and 722 nm) are detected. The shoulder band is produced as a result of 1s, 4d transition¹⁴. It was exhibited as of now in early work in literature^{15,16} that exchange coupling of the metal center with ligand states offers to ascend to turn permitted spin transitions at low energy.

It will be demonstrated that there are bands in the region of 416-429 nm beneath the Q-band excitation for metal (1,4-dithin)porphyrzines. These states arise from d-d excitations and ligand metal exchange coupling. It has been recommended that both energy band Q and energy band B can be impacted by the metal-to-ligand charge-exchange groups¹⁷. Consequently, the sensitization of the synthesized (1,4-dithin)porphyrzines could develop the absorbance range in the visible region.

NMR and molecular mass estimations of the prepared compounds

With respect to the structure of 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-2,3-dicarbonitrile **3**, the ¹H-NMR spectrum of **3** revealed band at 1.86 assignable to CH₃ group. The ¹³C NMR spectrum show bands at 9.1, 117.8, 125.1, 157.8, 159.4 and 186.9 related to the assigned structure of compound **3**. Elemental analytical data of new dinitrile **3** is in agreement with its structure (see experimental, scheme 1).

The ^1H -NMR spectrum of metal free (1,4-dithin)porphyrazine 2H-Pz **4a** predicts one signal at $\delta = 3.8$ and 1.81 related to NH and CH_3 protons. The existence of signal related to NH protons in the ^1H -NMR spectrum of 2H-Pz **4a** gives coordinate proof of the development of an unsymmetrical tetra-dentate ligand. ^{13}C -NMR spectrum of 2H-Pz **4a** showed a band at 8.8 , 116.9 , 126.8 , 140.5 , 154.3 , 158.3 , 159.2 , and 165.4 , 187.7 which confirm the structure of the porphyrazine.

Elemental basic examinations of the arranged porphyrazines demonstrate that the measure of carbon atoms inside their structures is predictable with their glorified structures illustrated in scheme 1.

The trial estimations of carbon atoms of the arranged porphyrazines are predictable with that computed for the normal structure. Additionally, the trial estimations of metal content (see experimental) of the arranged porphyrazines are predictable with that figured for the normal porphyrazines equations. Also, metal content (see experimental) and atomic masses of the prepared porphyrazines affirm the productivity of cyclo-tetramerization and complexation reactions.

Catalytic Activity of the Prepared Porphyrazines

Thiols are found in many industrial wastes. Thiols can be oxidized to water-insoluble disulfides which form an oily layer and can be easily separated. The prepared (1,4-dithin)porphyrazines **4a** - **4d** were used as efficient catalysts for the oxidation of thiophenol and benzyl thiol to their disulfides in the presence of air atmosphere.

BET surface areas of the synthesized porphyrazine catalysts are shown in Table 1. Nitrogen adsorption measurements show that the materials have considerable surface areas in the range from $433 \text{ m}^2\text{g}^{-1}$ to $458 \text{ m}^2\text{g}^{-1}$ with high adsorption at low relative pressure ($P/P_0 < 0.02$) showing microporosity¹⁸. Small differences have been observed in the metal-Pz BET surface areas. The results of oxidation of thiophenol and benzyl thiol show that after 20 minutes the highest yield of the corresponding disulfides reached 93% and 90%, respectively (see Experimental).

Thus, metal-pyrazinoporphyrazines are far more effective catalysts for the oxidation of thiols

indicating the influence of the presence of donating methyl groups on the progress of the catalytic process. As expected, quinone moieties along the backbone of the porphyrazine were found to be effective in the pathway of catalytic process¹⁹. Spectral analysis of the used catalyst after the completion of the reaction showed that the catalyst containing quinone rings was transformed to a catalyst containing quinol rings as a result of oxidation of thiols. IR spectra of the used porphyrazine catalyst showed the disappearance of the band related to (C=O) group and appearance of the broadband at 1650 and 3392 cm^{-1} assignable to phenolic group assuring oxidation process.

Also, the ^1H -NMR (CDCl_3) of the used catalyst shows multiple bands at 7.66 - 7.84 and broad singlet band at 11.42 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 logic to accept that the oxidation of phenol by molecular oxygen is essentially an electrophilic reaction and the rate constraining advance is the reaction between the aryloxy radical with oxygen^{20,21}.

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. Reusability of the quinolinic catalyst can be achieved through oxidation of the phenolic groups in the presence of air oxygen²², and then can be subjected to a second run of the oxidation reaction with the same substrate affording converged products of disulfides and catalyst with quinone structure.

Thus the prepared catalysts **4a-4d** can be reused several times. Yield percentage of disulfides obtained by oxidation catalytic process shows that metal porphyrazine catalysts indicate higher catalytic activity in comparison with the metal-free porphyrazine catalyst. We found that the activity of the complexes is affected not only by the nature of the complex-forming metal but also by the BET surface area values of the porphyrazine catalysts. The pure diphenyl disulfide and dibenzyl disulfide were obtained after 20 minutes with an average yield for all catalysts around 93% and 90%, respectively.

CONCLUSIONS

2,3-Dichloro-5,6-dimethylbenzoquinone through condensation reaction with di(sodiothio)maleonitrile produced hetero-cyclic thianone, 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithine-2,3-dicarbonitrile. The dicarbonitrile product was cyclo-tetramerized using lithium/pentanol and acetic acid affording the corresponding tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrizine (2H-Pz). Also, the dicarbonitrile compound was cyclo-tetramerized using metal salt and quinoline affording the corresponding tetra 6,7-dimethyl-5,8-dioxo-5,8-dihydro-1,4-benzodithin-porphyrizinato-metal II (M-Pz), M = Co, Ni or Zn. The photoactivity of the synthesized porphyrizines was stretched out to the visible light. They are effective sensitized catalysts for the completely photocatalytic oxidation of thiophenol and benzyl thiol to their water-insoluble disulfides (with an average yield of 93% and 90% respectively) in the presence of air atmosphere in wastewater in 20 minutes.

ACKNOWLEDGMENTS

The authors are pleased to thank Taif University, Saudi Arabia for providing the facilities for this research (Research project number: 4872-437).

REFERENCES

- [1] Tuncer, S.; Koca, A.; Gül, A.; Avciata, U. Synthesis, characterization, electrochemistry, and spectroelectrochemistry of novel soluble porphyrizines bearing unsaturated functional groups. *Dyes Pigm.* **2011**, *92*, 610-618.
- [2] Deng, K.; Huang, F. A novel catalyst Iron (II) Tetra (1,4-dithin) porphyrizine for oxygenating degradation of organic pollutants in aqueous solutions. *ChemInform* **2004**, *33*, 34-35.
- [3] Abdel-Razik, H. H.; El-Sayed, S.; Hassen, A. Dielectric properties of new fully conjugated 2H- and metal-pyrazinoporphyrazine network polymers. *J. Appl. Polym. Sci.* **2011**, *121*, 3579-3589.
- [4] Zhang, Z.; Zhang, M.; Deng, J.; Deng, K.; Zhang, B.; Lv, K.; Sun, J.; Chen L. Photocatalytic oxidative degradation of organic pollutant with molecular oxygen activated by a novel biomimetic catalyst ZnPz (dtn-COOH)₄. *Appl. Catal., B.* **2013**, *132-133* (27), 90-97.
- [5] Chen, L.; Zhang, Z.; Wang, Y.; Guan, Y.; Deng, K. Photocatalytic properties and electrochemical characterization of a novel biomimetic oxygenase enzyme photocatalyst iron (II) tetrahydroxy-methyl tetra (1,4-dithin) porphyrizine for the degradation of organic pollutants. *J. Mol. Catal. A: Chem.* **2013**, *372*, 114-120.
- [6] Tang, J.; Chen, L.; Sun, J.; KangleLv K.; Deng, k. Synthesis and properties of iron(II) tetra(1,4-dithin)porphyrizine bearing a peripheral long-chain alkyl group of active end-bromine. *Inorg. Chem. Commun.* **2010**, *13*, 236-239.
- [7] Xiao-mei, R.; Bing-guang, Z.; Ke-jian, D. The Synthesis of tri (pentyloxy) phenyl-(1,4-dithin) porphyrizines. *Guangzhou Chem Ind.* **2015**, *11*, 81-82.
- [8] Abdel-Razik, H. H.; Asghar, B. H. Synthesis, characterization and spectroscopic investigation of novel pyrazinoporphyrazine network polymer-supported metal (ii) based catalysts. *Chin. J. Polym. Sci.* **2013**, *31*, 242-250.
- [9] Joglekar, H. S.; Samant, S. D.; Joshi, J. B. Kinetics of wet air oxidation of phenol and substituted phenols. *Water Res.* **1991**, *25*, 135-145.
- [10] Bruder, I.; Schöneboom, J.; Dinnebier, R.; Ojala, A.; Schäfer, S.; Sens, R.; Erk, P.; Weis, J. What determines the performance of metal phthalocyanines (MPc, M = Zn, Cu, Ni, Fe) in organic hetero-junction solar cells? A combined experimental and theoretical investigation. *Org. Electron.* **2010**, *11*, 377.
- [11] Kim, J.; Jaung, J. Y.; Ahn, H. Tetra pyrazinoindoloporphyrazine Langmuir-Blodgett films. *Macromol. Res.* **2008**, *16*, 367-372.
- [12] Jaung, J. Y.; Matsuoka, M.; Fukunishi, K. Syntheses and characterization of push-pull tetrapyrazino [2,3-b] indoloporphyrazines. *Synthesis* **1998**, 1347-1351.
- [13] Puigdollers, J.; Voz, C.; Fonrodona, M.; Cheylan, S.; Stella, M.; J. Andreu, J.; Vetter, M.; Alcubilla R. Copper

- phthalocyanine thin-film transistors with the polymeric gate dielectric. *J. Non-Cryst. Solids***2006**, *352*, 1778-1782. [20]
- [14] Wizel, S.; Margel, S.; Gedanken, A.; Rojas, T. C.; Fernández, A.; Prozorov, R. [21] The preparation of metal-polymer composite materials using ultrasound radiation: part II. Differences in physical properties of cobalt-polymer and iron-polymer composites. *J. Mater. Res.***1999**, *14*, 3913-3920. [22]
- [15] Schneboom, J.; Dinnebier, R. What determines the performance of metal phthalocyanines (MPc, M=Zn, Cu, Ni, Fe) in organic heterojunction solar cells? A combined experimental and theoretical investigation. *Org. Electron.***2010**, *11*, 377-387.
- [16] Cory, M. G.; Zerner, M. C. Metal-ligand exchange coupling in transition-metal complexes. *Chem. Rev.***1991**, *91*, 813-822.
- [17] Chen, Q.; Gu D.; Gan, F. Ellipsometric spectra of cobalt phthalocyanine films. *Phys. B***1995**, *212*, 189.
- [18] McKeown, N. B.; Makhseed, S.; Budd, P. M. Phthalocyanine-based nano-porous network polymers. *Chem. Commun.* **2002**, 2780.
- [19] Arai, H.; Yashiro, M. Catalytic oxidation of ethylene using functional quinone-polymer-anchored palladium catalysts. *J. Molec. Catal.***1978**, *3*, 427.
- Joglekar, H. S.; Samant, S. D.; Joshi, J. B. Kinetics of wet air oxidation of phenol and substituted phenols. *Water Res.***1991**, *25*, 135-145.
- Sadana, A.; Katzer, J. Involvement of free radicals in the aqueous phase catalytic oxidation of phenol over copper oxide, *J. Catal.* **1974**, *35*, 140.
- Hay, A. S. (1967) Aromatic polyethers. In: Fortschritte der Hochpolymeren-Forschung. Advances in Polymer Science, Vol 4/4. Springer, Berlin, Heidelberg.

Table-1: Spectral data of the prepared compounds

Comp. No.	M.P. (°C)	BET area (m ² /g ⁻¹)	IR (KBr) vcm ⁻¹					U.V (CHCl ₃) λmax nm	
			C=O	C=N	C=C	CN	NH	Soret band	Q band
3	145	-----	1667	----	1602	2224	----	----	----
4a	183	458	1686	1522	1616		3335	342	637, 708
4b	209	433	1677	1508	1606		----	329, 416	642, 723
4c	216	439	1679	1514	1609		----	325, 423	648, 718
4d	212	437	1681	1512	1607		----	322, 429	652, 726

Scheme 1. Synthetic Pathway of Tetra(1,4-dithin)Porphyrazines