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Synthesis of Phthalocyanine derivatives by synergistic effect of catalysts over nanodimensional zeolites under solvent-free conditions

ABSTRACT

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Copper (II) phthalocyanine and 2,9,16,23 tetrakis nitro copper (II) phthalocyanine has been synthesized respectively from phthalonitrile and 4-nitro phthalonitrile under solvent-free condition using two different catalysts over nanodimensional zeolites. 4-Nitro phthalonitrile synthesized from phthalimide in three steps. The newly prepared compounds have been characterized by IR, UV-Vis, ¹HNMR and MS spectra.

Keywords: *Nanodimensional; Zeolite; Catalyst; Phthalocyanine; Solvent-free.*

INTRODUCTION

Phthalocyanines (Pcs) have macrocyclic 18 π electron systems that are known to be the source of semiconductor characteristics, and they are characterized by high thermal and reasonable chemical stability [1-2]. Phthalocyanines show interesting photophysical properties and both photo and dark semiconductivity, which makes them particularly interesting for use in more advanced technological applications, such as optical recording, non-linear optics, light emitting diodes, a basis for optical sensing, photodynamic therapy and gas sensors [3-4]. One of the goals of catalysis researchers in recent times has been the synthesis of inorganic compounds. One approach has been the encapsulation of transition metal complexes inside the cages and void spaces of nanodimensional zeolite and zeolitic materials the porous inorganic mantle zeolite, Providing hopefully. The right steric requirement for the metal complexes and imposing certain restrictions (based on size and shape) to the access of the active site have been done by the substrate molecules [5-6]. The main advantages of using nanodimensional zeolites are that they are environmentally benign, can be reused and are thermally stable. Protonated forms of nanodimensional zeolites have been found to be efficient catalysts in reactions [7-12].

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EXPERIMENTAL

The UV-Vis spectra were measured on a Shimadzo UV 160A spectrometer. The ^1H NMR (500MHz) spectra were obtained with Bruker 400, 500 DRX-Avance NMR. The IR spectra were taken with a Shimadzo 470 spectrometer using KBr pellets. Melting points of crystalline dicyano compounds were measured with an electrothermal melting point apparatus. Mass spectra were recorded on a GC-MS Agilent Technologies QP-5973N MSD instrument.

Synthesis of 4-nitro phthalimide

To 25mL of a mixture of concentrated sulfuric acid and nitric acid at 15°C was added (0.027mol, 4g) phthalimide with stirring. The temperature was raised slowly to 35°C and held for 1.5h (Scheme1). The product cooled to 0°C and poured into 40g of ice and collected by vacuum filtration. Yield: 70%, 3.88g; mp: 195°C ; IR(KBr, v/cm^{-1}): 3200 s, 3050 w, 1730 s, 1620 w, 1600 w, 1540 s, 1462 m, 1400 m, 1345 s, 860 m, 795 s, 715 cm^{-1} .

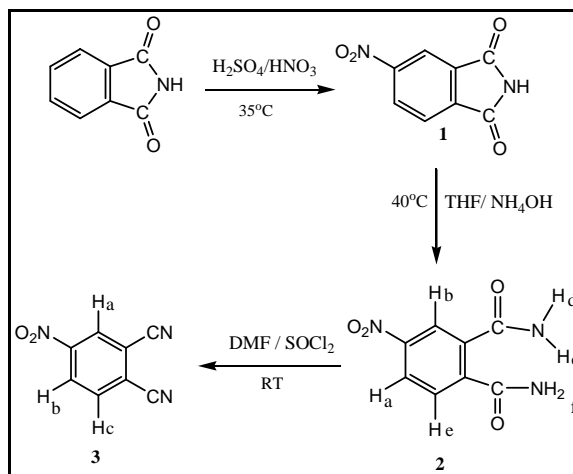
Synthesis of 4-nitro phthalimide

To 10mL of THF was added (0.005mol, 1g) of 4-nitro phthalimide and the mixture was heated to 40°C and 7mL ammonium hydroxide was added to the solution with stirring for 2h (Scheme1). The product collected by filtration. Yield: 75%, 0.78g; mp: 197°C ; IR(KBr, v/cm^{-1}): 3400 s, 3300 m, 3100 w, 1665 s, 1605 m, 1525 s, 1475 m, 1400 w, 1345 s, 1125 m, 860 s, 790 s, 740 cm^{-1} ; ^1H NMR (500 MHz, DMSO, ppm) δ : 8.31 (dd, $J=8.35\text{Hz}$, $J=2.3\text{Hz}$, 1H, H_a), 8.28 (d, $J=2.2$, 1H, NH, H_b), 8.03 (s, 1H, NH, H_c), 7.97 (s, NH, 1H, H_d), 7.70 (d, $J=8.33\text{Hz}$, 1H, H_e), 7.60 (br.s, 2H, NH_2 , H_f) ppm.

Synthesis of 4-nitrophthalonitrile

To 7mL of dry DMF at 0°C and a CaCl_2 drying tube was slowly added 0.73mL of thionyl chloride and (0.0048mol, 1g) of 4-nitro phthalimide in portion over a 10-min period. The reaction stirred for 3h at room temperature (Scheme1). The reaction mixture was stirred into 20mL ice and collected by vacuum filtration. Yield 90%, 0.75g; mp: 142°C ; IR (KBr, v/cm^{-1}): 3080 w, 2220 m, 1600 m, 1532 s, 1350 s, 865 s, 795 s, 740 cm^{-1} ;

^1H NMR (500 MHz, DMSO, ppm) δ : 9.05 (d, $J=2.4\text{Hz}$, 1H, H_a), 8.69 (dd, $J=8.8\text{Hz}$, $J=2.4\text{Hz}$, 1H, H_b), 8.45 (d, $J=8.8\text{Hz}$, 1H, H_c) ppm.



Scheme 1. Synthetic route of 4-nitro phthalonitrile

Preparation of nanodimensional Zeolites

The sodium form of nanodimensional zeolites was calcined in air at 873 K for 5 h to decompose the organic templates. The resulting Na^+ ions was exchanged by NH_4^+ ions from a 1M NH_4NO_3 solution at 353 K for 10 h, using a liquid/solid ratio of 100 mL per gram of zeolite. Then, the nanodimensional zeolites were separated from the solution by filtering and were thoroughly washed. The exchange procedure was repeated three times to complete the Na^+ ion exchange. Subsequently, the catalysts was dried overnight at 383 K and calcined in flowing dry air at 773 K for 5 h to produce the acidic form of the zeolites (HZSM-5 and H β) (Table 1).

Table 1. Main structural characteristic of zeolites

Zeolite	Si/Al	Area (m^2g^{-1})	Crystallite size (μm)
HZSM-5	40	420	1.0-3.0
H β	15	582	0.02-0.03

Synthesis of copper (II) phthalocyanine derivatives (4). A general procedure

In this paper we synthesized phthalocyanine derivatives in the presence of ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$), ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ catalysts over nanodimensional zeolites. We mixed (4mmol) of phthalonitrile derivatives, (1mmol, 0.17g) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as first catalyst and 5% W ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) as a second catalysts using 10%W H β or HZSM-5 nanodimensional zeolites as third catalysts. The mixture heated with stirring to 130 °C -145°C and solid washed with boiling water (Scheme2) (Table2). The dark blue solids were purred with dichloromethane and acetone. The solids were dissolved in DMSO and nanodimensional zeolites filtered. Solved products in DMSO separated by

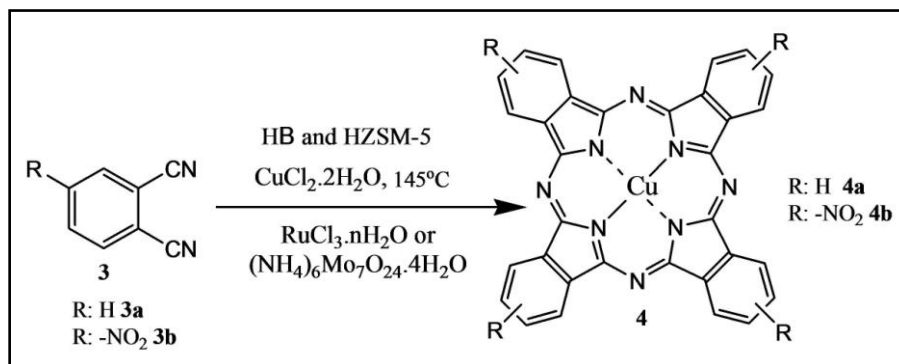
distillation. Products analyzed by IR, MS and UV-Vis spectra.

Copper (II) phthalocyanine (4a)

IR (KBr, ν/cm^{-1}): 3040 w, 1647 m, 1600 m, 1475 w, 1322 s, 895 w, 750 m, 720s cm^{-1} ; UV-Vis (DMSO) $\lambda_{\text{max}} = 335\text{nm}$ (S band) ($\log\epsilon=0.766$), 641nm (Q band) ($\log\epsilon=0.380$); Exact mass (M^+): calcd. For $\text{C}_{32}\text{H}_{16}\text{CuN}_8$, 576.08 found 576.08.

22,9,16,23 Tetrakis nitro copper (II)phthalocyanine (4b)

IR (KBr, ν/cm^{-1}): 3100 w, 1680 m, 1610 m, 1520 s, 1335 s, 900 m, 845 s, 755 s cm^{-1} ; UV-Vis (DMSO) $\lambda_{\text{max}} = 630\text{nm}$ (Q band) ($\log\epsilon=0.346$), 356nm (S band) ($\log\epsilon=0.428$); Exact mass (M^+): calcd. For $\text{C}_{32}\text{H}_{12}\text{CuO}_8\text{N}_{12}$, 756.07 found 756.07.



Scheme 2. Synthetic route of phthalocyanine derivatives

Table 2. Synthesis of copper (II) phthalocyaninederivatives over nanodimensional zeolites

Entry	Precursor (4mmol)	Catalysts	Zeolite	Time (min)	Yield (%)	Colour	Mp (°C)
4a	3a, (0.51g)	$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	HZSM-5	35	90, 0.5g	blue dark	upper 350
4a	3a, (0.51g)	$(\text{NH}_4)_6\text{Mo}_{24} \cdot 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	H β	60	75, 0.43g	blue dark	upper 350
4b	3b, (0.69g)	$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	HZSM-5	20	95, 0.72g	blue dark	upper 350
4b	3b, (0.69g)	$(\text{NH}_4)_6\text{Mo}_{24} \cdot 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	H β	50	80, 0.60g	blue dark	upper 350

Synthesis of metal-free phthalocyanine derivatives (5). A general procedure

For synthesis of these products the synthesized phthalocyanines (0.5mmol) dissolved in minimum amount of trifluoro acetic acid at room temperature with argon gas and stirred for 3h then the product poured into ice-water mixture and neutralized with 25% ammonia solution. The solid was filtered by vacuum pump and washed with water (Scheme 3).

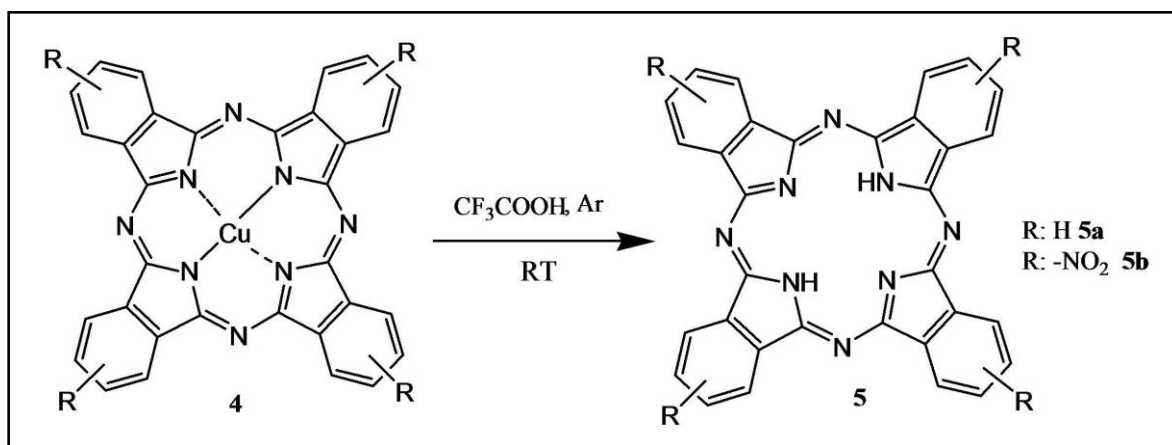
- **Metal-free phthalocyanine (5a)**

Dark blue; yield: 82%, 0.21g; IR (KBr, ν/cm^{-1}): 3320 m, 3040 w, 1647 m, 1600 m, 1475 w,

1322 s, 895 m, 750 m, 720 m cm^{-1} ; UV-Vis (DMSO) $\lambda_{\text{Max}}= 698\text{nm}$ (Q_x band) ($\log\epsilon=0.421$), 668nm (Q_y band) ($\log\epsilon=0.402$), 321nm (S band) ($\log\epsilon=0.571$); Exact mass (M^+): calcd. For $C_{32}H_{18}N_8$, 514.54 found 514.53.

- **2,9,16,23 Tetrakis nitro phthalocyanine (5b)**

Dark blue; yield: 87%, 0.30g; IR(KBr, ν/cm^{-1}): 3325 s, 3100 w, 1680 m, 1610 s, 1520 s, 1335 s, 900 m, 845 m, 755 cm^{-1} ; UV-Vis (DMSO) $\lambda_{\text{Max}}= 668\text{nm}$ (Q_x band) ($\log\epsilon=0.439$), 619nm (Q_y band) ($\log\epsilon=0.451$), 348nm (S band) ($\log\epsilon=0.536$); Exact mass (M^+): calcd. For $C_{32}H_{14}O_8N_{12}$, 694.52 found 694.53.



Scheme 3. Synthetic route of metal-free phthalocyanine derivatives

RESULTS AND DISCUSSION

The synthesis time of copper (II) phthalocyanine derivatives in the presence of ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) as Lewis acid and HZCM-5 catalysts was very shorter than ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) and H β nanodimensional zeolite. Moreover, its yield was very higher than another (Table 2). The peak at 620–690 nm (Q-band) attributed to the $\pi-\pi^*$ transition and the peak at 330–380 nm (S-band) ($n-\pi^*$). In IR spectra, peak elimination of nitrile group in (2230cm^{-1}) and appearance of peak of $\text{C}=\text{N}$ identified the synthesis of products. In UV-Vis spectra of these compounds (D_{4h} symmetry) was observed two strong absorbance at 620-690nm (Q band) and 330-380nm (S band). The Q band attributed to electronic transition from HOMO to LUMO and S band from HOMO-1 to LUMO. In

metal-free UV-Vis spectra of these compounds (D_{2h} symmetry) was observed three absorbance at (Q_x band), (Q_y band) and (S band). UV-Vis absorption spectra of the metal-free phthalocyanines exhibited the split of Q band, which is characteristic of metal-free phthalocyanines. The peak at Q_x band attributed to electronic transition from HOMO to LUMO and Q_y band from HOMO to LUMO+1. The S band attributed to electronic transition from HOMO-1 to LUMO.

CONCLUSIONS

The low activity of H β , a small pore bidirectional nanodimensional zeolite, is probably related to diffusional limitations of the pores and geometrical constraints for the formation of the

intermediates inside the pores (Table 1). If catalyst decay is related to a strong adsorption of reactant or products, we have to expect that when the reaction temperature is increased; the adsorption constant, and therefore the amount of reactants and adsorbed products should decrease, decreasing the catalyst decay.

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REFERENCES

- [1] Zhao, P., Song, Y., Dong, S., Niu, L., Zhang, F. (2009). Synthesis, photophysical and photochemical properties of amphiphilic carboxyl phthalocyanine oligomers, *Dalton Trans*, 32, 6327-6334.
- [2] Bilgin, A., Yag, C., Mendi, A., Yıldız, U. (2007). Synthesis and characterization of new polymeric phthalocyanines substituted with diaza-18-crown-6 macrocycles through ethyleneoxy bridges, *Polyhedron*, 26, 617-625.
- [3] Wang, K., Qiang, F., Jicheng, M., Zhao, B. (2012). Synthesis and electrochemical properties of a series of novel tetra(4-benzoyl)phenoxyphthalocyanine derivatives, *Sci. China Chem*, 55, 1872-1880.
- [4] Karaoğlu, H., Pekbelgin, R., Koca, A., Imath, F., (2012). Synthesis, electrochemical and spectroelectrochemical characterization of novel soluble phthalocyanines bearing chloro and quaternizable bulky substituents on peripheral positions, *Dyes Pigm.*, 92, 1005-1017.
- [5] Rajesh, K.R., Menon, C.S., (2005). Determination of conduction parameters of vacuum deposited magnesium phthalocyanine thin films from their electrical, optical studies and application of VRH model, *J. Non-Cryst. Solids*, 351, 2414-2420.
- [6] Eichhorn, H., (2000). Mesomorphic phthalocyanines, tetraazaporphyrins, porphyrins and triphenylenes as charge-transporting materials, *J. Porphy. Phthalocya.*, 4, 88-102.
- [7] Gemma C. S., Gokhan Y., Johanna K., Lionel, R. M., John M. S., (2009) Synthesis and phase behaviour of β -octaalkylporphyrins, *J. Mater. Chem.*, 19, 1051-1060.
- [8] Leanne, B. J., Ross, W. B., (2012) Unique Diagnostic and Therapeutic Roles of Porphyrins and Phthalocyanines in Photodynamic Therapy, Imaging and Theranostics, *Theranostics*; 2(9):916-966.
- [9] Mohamed A., Raymond L.M., Sharif A., Alina V., Bertrand D., Daniel G.S., Holger E., (2010). Halide effect in electron rich and deficient discotic phthalocyanines, *J. Mater. Chem.*, 20, 627-633.
- [10] Eichhorn, H., (2000). Mesomorphic phthalocyanines, tetraazaporphyrins, porphyrins and triphenylenes as charge-transporting materials, *J. Porphy. Phthalocya.*, 4, 88-102.
- [11] Barbara A. Bench, Andrew Beveridge, (2002) Wesley M. Sharman, Gerald J. Diebold, Johan E. van Lier, Sergiu M. Gorun, *Angewandte Chemie-international Edition-ANGEW CHEM INT ED*, 41(5), 35-46.
- [12] Durmus, M., Ahsen, V., (2010). Photophysical and Photochemical Properties of Fluorinated and Nonfluorinated n-Propanol-Substituted Zinc Phthalocyanines, *Eur. J. Inorg. Chem.*, 3, 1220-1230.

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