

**ANNEXURE - VIII**

**UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI-110 002**

**PROFORMA FOR THE SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE  
FINAL REPORT OF THE WORK DONE ON THE PROJECT**

<b>1. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR</b>	<b>Dr. Pulakesh Bera 154/3 Mohendra Bhattacharya Road, Sibpur, Howrah, West Bengal - 711104</b>
<b>2. NAME AND ADDRESS OF THE INSTITUTION</b>	<b>Panskura Banamali College P.O. Panskura R S, Dist.-Midnapore (East), West Bengal - 721152</b>
<b>3. UGC APPROVAL NO. AND DATE</b>	<b>(i) F. No. 42-280/2013 (SR) Dated-12/03/2013 (ii) F. No. 42-280/2013 (SR) Dated-23/03/2016</b>
<b>4. DATE OF IMPLEMENTATION</b>	<b>01-04-2013</b>
<b>5. TENURE OF THE PROJECT</b>	<b>Initially 3 years and extended for one additional year without any financial support</b>
<b>6. TOTAL GRANT ALLOCATED</b>	<b>Rs.9,40,284/- (Rupees Nine lacs forty thousand and two hundred eighty four only)</b>
<b>7. TOTAL GRANT RECEIVED</b>	<b>Rs.8,66,336/-(Rupees eight lacs sixty six thousand and three hundred thirty six only)</b>
<b>8. FINAL EXPENDITURE</b>	<b>Rs. 9,43, 607/-(Rupees Nine lacs forty three thousand six hundred and seven only)</b>
<b>9. TITLE OF THE PROJECT</b>	<b>“Design, Development and Characterization of Mesoporous Functional Metal-Organic Framework (MOF)”</b>
<b>10. OBJECTIVES OF THE PROJECT</b>	<b>Annexure - I</b>
<b>11. WHETHER OBJECTIVES WERE ACHIEVED (GIVE DETAILED)</b>	<b>Annexure - II</b>
<b>12. ACHEIVEMENTS FROM THE PROJECT</b>	<b>Annexure - III</b>
<b>13. SUMMARY OF THE FINDINGS (IN 500 WORDS)</b>	<b>Annexure - IV</b>

15. WHETHER ANY PH.D ENROLLED/  
PRODUCED OUT OF THE PROJECT TWO

16. NO. OF PUBLICATIONS OUT OF THE  
PROJECT (PLEASE ATTACHED REPRINTS) Six (Please see the attachments)



Principal Investigator

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Co-Investigator



Principal

Principal  
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07 APR 2017



## Annexure-I

### OBJECTIVES OF THE WORK


Our objectives have centered on the following: (a) rational design of organic SBUs in such a way that the SBUs limit its catenation and form permanent nanoscale porosity upon coordination with suitable metal ions, (b) rapid and quality separation of desired MOFs from contaminants that generated during synthesis, and (c) use of MOFs for chemical separation, chemical catalyst and nanoparticle synthesis using the prepared MOFs as sacrificing molecular precursor or block compound. The traditional experiments in coordination chemistry rely on mostly structure-activity relationship that certainly benefit the scientific community and society but have less technological applications. The application oriented research on coordination chemistry must open a new avenue in future for the benefit of the society.

  
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**Annexure – II****WHETHER OBJECTIVES WERE ACHIEVED (GIVE DETAILED)**

The primary objectives of the work are the synthesis of Metal-Organic Frameworks (MOF) using SBU (secondary Building Units) and organic linkers. The judicious choice of both SBU and linker must be matched to produce a MOF in true sense. In accordance to the objectives laid down in the project, basic syntheses of secondary building unit (SBU) are successful. The synthesis and systematic characterization are made before going to further reactions. So far we are able to synthesize more than ten new SBU (ligand) (scheme-1). After careful consideration, these newly made SBU ligands are allowed to react with several metal salt in absence of organic linker group to check whether the ligand itself fulfill the function of a linker group. Most of the cases the metal-organic compounds are formed which are devoid of the qualities of true MOFs. Simultaneously, the SBU/ligands are also reacted with metal salts in the presence of linker organic molecules (non-carboxylic category). Several attempts are made to form the true MOF with the diazole SBU and linker molecules. However, the metal-organic compounds are prepared from the reaction between newly made ligands and several metal salts. These are thoroughly characterized through the available tools. Various applications such as catalytic activities towards several dyes degradation, *in vitro* catecholase mimicking activities, DNA cleavage activity, cell cytotoxicity measurements, preparation of various nanoparticles using new compounds as single-source precursor (SP) and photovoltaic application are experimented.

Further work on the as synthesized compounds such as post synthesis modification with suitable linker molecule needs to be explored for quality MOFs.

  
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### Annexure –III

#### ACHEIVEMENTS FROM THE PROJECT

The major achievements during the project are given below


Nine students completed their project work for the purpose of the partial fulfillment for the Degree of Master in Chemistry from the Department of Chemistry, Panskura Banamali College.

Two students (Ananyakumari Santra and Pradip Bera) enrolled themselves for the Degree of Doctor of Philosophy in the subject Chemistry under Vidyasagar University.

Collaboration with different research institutes in India (three) and abroad (two) with Panskura Banamali College.

Ten new compounds with various applications are obtained and reported in peer reviewed journals. Few works are in progress and will appear in the referred Journals.

Last but not the least the merit of elements of the project contributed momentum to (i) the “A” grade NAAC accreditation (2016-2021) and (ii) recommendation of Fund for Improvement of S&T Infrastructure (FIST)(Level-0, 2016) from Government of India of the college. The college emerges as potential research centre under the affiliating university.

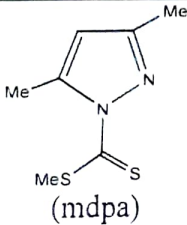
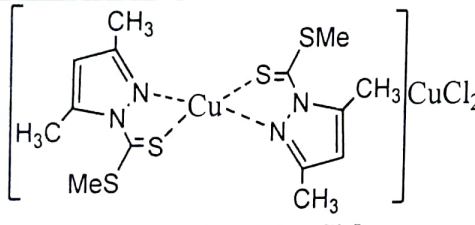
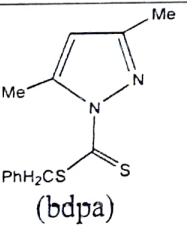
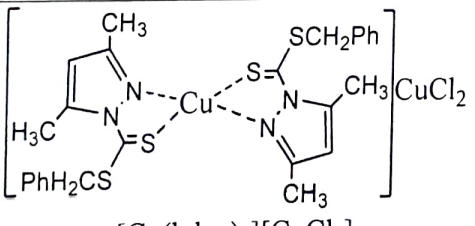
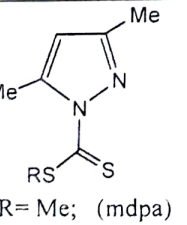
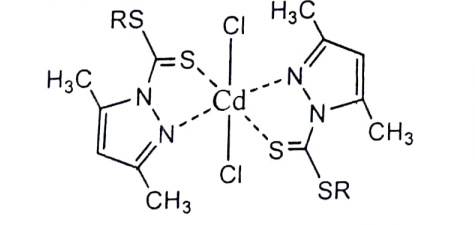
  
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## Annexure-IV

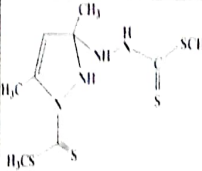
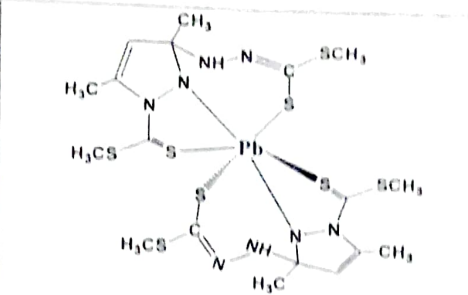
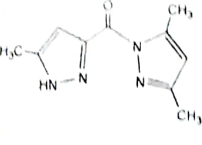
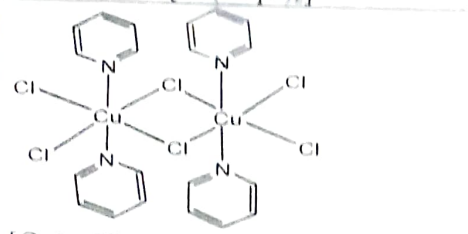
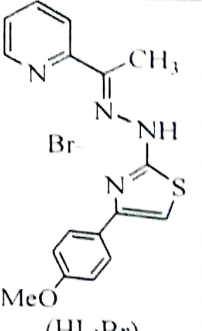
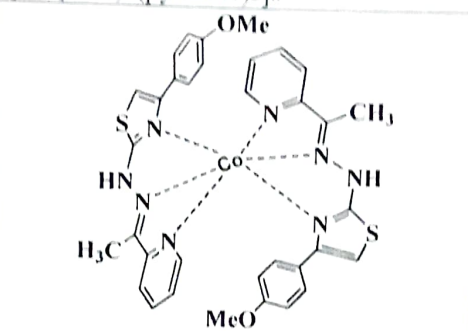
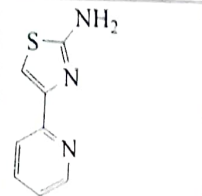
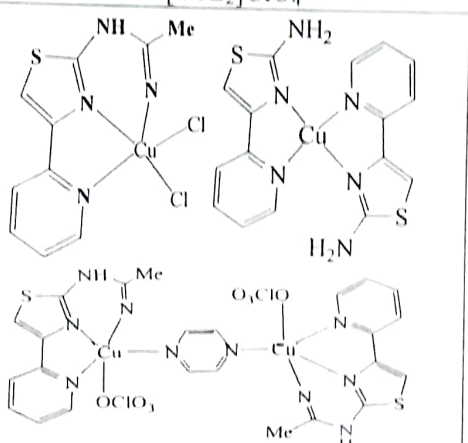
## SUMMARY OF THE FINDINGS (IN 500 WORDS)

In a comprehensive effort to develop new pyrazole based ligands and the Metal-organic compounds hitherto we are able to synthesize six new pyrazole and one new thiazole derivatives. We also successfully synthesized twenty five metal-organic complexes from the new ligands. All the ligands are thoroughly characterized by the available means such as IR, NMR, Mass and CHN analysis. The derived metal complexes are also characterized through available means like single X-ray crystallography, Thermogravimetry, cyclovoltammetry, EPR, FTIR spectroscopy. Scheme-1 represents the information of the work done so far with the new ligands and their metal complexes and their applications.

**Scheme-1: Synthesized Metal-organic complexes from various new Ligands and their Applications**

Sl. No.	Organic ligands	Metal organic complexes	Applications	Ref.
1.	 <p>(mdpa)</p>	 <p><math>[Cu(mdpa)_2][CuCl_2]</math></p>	<ul style="list-style-type: none"> <li>• Application in <math>Cu_2S</math> nanoparticles synthesis</li> <li>• Dye degradation study</li> <li>• Catechol oxidase mimetic activity</li> <li>• Thin films</li> </ul>	[1] [1] [2] [3]
2.	 <p>(bdpa)</p>	 <p><math>[Cu(bdpa)_2][CuCl_2]</math></p>	<ul style="list-style-type: none"> <li>• Application in <math>Cu_xS</math> (<math>x=2</math> or 1.97) nanoparticles synthesis</li> <li>• Catechol oxidase mimetic activity</li> </ul>	[4] [2]
3.	 <p>R= Me; (mdpa) CH<sub>2</sub>Ph; (bdpa)</p>	 <p>R=Me; <math>[Cd(mdpa)_2Cl_2]</math> CH<sub>2</sub>Ph; <math>[Cd(bdpa)_2Cl_2]</math></p>	<ul style="list-style-type: none"> <li>• Application in CdS nanoparticles synthesis and photodegradation of Dye</li> </ul>	[5]


  
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4.	 <p>(Hmdpc)</p>	 <p>[Pb(mdpce)<sub>2</sub>]</p>	<ul style="list-style-type: none"> <li>• Application in PbS nanoparticles synthesis</li> <li>• Photocatalytic activity</li> </ul>	[6]
5.		 <p>[Cu(μ-Cl)<sub>2</sub>(pyridine)<sub>2</sub>]<sub>n</sub></p>	<ul style="list-style-type: none"> <li>• Antibacterial activity and anti-larval activity</li> </ul>	[7]
6.	 <p>(HL·Br)</p>	 <p>[CoL<sub>2</sub>]ClO<sub>4</sub></p>	<ul style="list-style-type: none"> <li>• Antibacterial activity and anti-larval activity</li> </ul>	Work in progress
7.			<ul style="list-style-type: none"> <li>• DNA interaction study</li> <li>• Cell cytotoxicity</li> <li>• LDH study</li> </ul>	Work in progress

The ligand mdpa (sl. no. 1) and bdpa (sl. no. 2) and their metal complexes were synthesized and characterized before applied them for several applications.

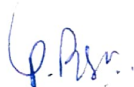
The single source precursor, [Cu(mdpce)]<sub>2</sub>[CuCl<sub>2</sub>] (sl. no. 1) derived from pyrazolyl dithiocarbamate ligand has been used to selectively synthesize hexagonal Cu<sub>2</sub>S nanoparticles in a

solvothermal process. The presence of the +1 oxidation state of copper is helpful for the selective synthesis of  $\text{Cu}_2\text{S}$ . The distorted shape, the tetrahedral complex of Cu(I) and the low decomposition temperature ( $100^\circ\text{C}$ ) facilitate the formation of flower-like hexagonal chalcocite ( $\text{Cu}_2\text{S}$ ) nanostructures with sufficient porosity and crystallinity in solvothermal process. Furthermore, the  $\text{Cu}_2\text{S}$  nanoparticles have also been used as catalyst for the photodegradation of aqueous solutions of Congo red (CR) with an efficiency of 90% as well as the reusable catalytic efficiency of  $\text{Cu}_2\text{S}$  is found to be 80% [1]. Further the complexes  $[\text{Cu}^{\text{I}}(\text{mdpa})_2][\text{Cu}^{\text{I}}\text{Cl}_2]$  (sl.no. 1) and  $[\text{Cu}^{\text{I}}(\text{L}_2)_2][\text{Cu}^{\text{I}}\text{Cl}_2]$  (sl. no. 2) exhibit prominent catechol oxidase activity in which a nice correlation, the easily oxidizable copper(I) center favoring the oxidation of 3,5-DTBC (3,5-ditertiary butyl catechol) is observed. Most importantly, these two compounds represent the class of copper(I) compounds that are rarely employed for the study of catecholase activity. The kinetics study exhibits a deuterium kinetic isotope effect in the catalytic oxidation of 3,5-DTBC by  $\text{O}_2$  as evidenced by about 1.9 times rate retardation in the deuterated solvent, suggesting the hydrogen atom transfer in the rate-determining step from the substrate hydroxy group to the metal-bound superoxo species [2]. Electrosynthesis of p- $\text{Cu}_2\text{S}$  thin films on a fluorine-doped tin oxide coated transparent conducting TCO ( $\text{SnO}_2:\text{F}$ ) glass substrate is carried out by chronoamperometry and cyclic voltammetry (CV) using an ethanolic solution of  $[\text{Cu}(\text{mdpa})_2][\text{CuCl}_2]$ . The appropriate potential at which the formation of stoichiometric p- $\text{Cu}_2\text{S}$  thin films occurs was found to be 0.48 V. The mechanism of the selective deposition of the p- $\text{Cu}_2\text{S}$  phase can be described by the electroreduction of Cu-N/S bonds in the coordination sphere following the dissociation of a precursor complex into Cu and mdpa. The free ligand mdpa is reduced to sulfide ion producing volatile organics in the electrochemical process. The quality deposition of thin films depends on the optimization of the SP concentration. An X-ray diffraction study reveals the high chalcocite phase of copper sulfide with preferential orientation along the (110) plane. The I-V characteristic of the as deposited  $\text{Cu}_2\text{S}/\text{TCO}$  thin film shows a non-ohmic behavior suggesting the formation of a p-n heterojunction diode. The p- $\text{Cu}_2\text{S}/\text{TCO}$  thin films are found to be excellent photocatalysts for the photo-degradation of Congo Red (CR) under visible light irradiation [3]. Hexagonal copper-deficient copper(I) sulfide ( $\text{Cu}_{2-x}\text{S}$ ,  $x = 0.03, 0.2$ ) nanocrystals are synthesized from  $[\text{Cu}(\text{bdpa})_2][\text{CuCl}_2]$  (sl. no2). The nucleation and growth of  $\text{Cu}_{2-x}\text{S}$  ( $x = 0.03, 0.2$ ) are effectively controlled by the SP and the solvent in the solvothermal decomposition process. During decomposition, fragment benzyl thiol ( $\text{PhCH}_2\text{SH}$ )

  
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from SP effectively passivates the nucleus leading to spherical nanocrystals. The chelating binders (solvent) like ethylene diamine (EN) and ethylene glycol (EG) prefer to form spherical Cu<sub>1.97</sub>S nanoparticles (djurleite), whereas nonchelating hydrazine hydrate (HH) shows the tendency to furnish hexagonal platelets of copper-deficient Cu<sub>1.8</sub>S. The optical band gap values (2.25–2.50 eV) show quantum confinement effect in the structure. The synthesized NCs display excellent catalytic activity (ca. 87 %) toward photodegradation of organic dyes like Congo Red (CR) and Methylene Blue (MB) [4]. Air-stable cadmium(II) complexes e.g., [Cd(mdpa)<sub>2</sub>Cl<sub>2</sub>] and [Cd(bdpa)<sub>2</sub>Cl<sub>2</sub>] were decomposed for the synthesis of CdS nanocrystals. The single-source precursors are used in the shape controlled synthesis of hexagonal CdS nanocrystals in solvothermal processes without using external surfactants. Complex 2, [Cd(mdpa)<sub>2</sub>Cl<sub>2</sub>], with the SCH<sub>3</sub> group in the structure always produced spherical CdS nanoparticles wherein the SP. [Cd(bdpa)<sub>2</sub>Cl<sub>2</sub>], with the SCH<sub>2</sub>Ph group selectively furnished rod-like CdS nanoparticles in the solvothermal reaction irrespective of the solvent used [5]. Visible light responsive PbS nanocrystals were synthesized from a pyrazole based precursor, [Pb(mdpc)<sub>2</sub>] (sl. No 4). High sulfur content in SP ensures quick passivation of PbS nanocrystal with thiol fragments. Thiol capped narrow band gap PbS nanocrystals itself shows superior visible light responsive catalytic activity than any other PbS composites like PbS-TiO<sub>2</sub>, PbS-graphene-TiO<sub>2</sub> etc. Moreover, reusability of the sample study shows comparable photocatalytic activity to the as synthesized PbS nanocrystals that provides a green approach to the removal of organic pollutants in Dye industries [6]. The mdpa, bdpa, copper(II)-mdpa, copper(II)-bdpa, cadmium(II)-mdpa, cadmium(II)-bdpa, Cu<sub>2</sub>S nanoparticles and CdS nanoparticles derived from different mdpa and bdpa complexes were screened towards antibacterial activities were evaluated against Gram positive bacteria including *Staphylococcus aureus* and *Bacillus subtilis* and Gram negative bacteria including *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae* and *Proteus vulgaris*. Fungi (*Candida albicans*, *Aspergillus flavus*) were also used to test antifungal activities [7].



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**References (Published Paper):**

- [1] Precursor-driven selective synthesis of hexagonal chalcocite ( $\text{Cu}_2\text{S}$ ) nanocrystals: structural, optical, electrical and photocatalytic properties, Gopinath Mondal, Pradip Bera, Ananyakumari Santra, Sumanta Jana, Tarak Nath Mandal, Anup Mondal, Sang Il Seok and Pulakesh Bera, **New J. Chem.**, **2014**, **38**, 4774-4782
- [2] Catechol oxidase mimetic activity of copper(I) complexes of 3,5-dimethyl pyrazole derivatives: Coordination behavior, X-ray crystallography and electrochemical study Ananyakumari Santra, Gopinath Mondal, Moumita Acharjya, Pradip Bera, Anangamohan Panja, Tarun K. Mandal, Partha Mitra, Pulakesh Bera, **Polyhedron**, **2016**, **113**, 5-13.
- [3] Single-source mediated facile electrosynthesis of p- $\text{Cu}_2\text{S}$  thin films on TCO ( $\text{SnO}_2:\text{F}$ ) with enhanced photocatalytic activities, Gopinath Mondal, Sumanta Jana, Ananyakumari Santra, Moumita Acharjya, Pradip Bera, Dipankar Chattopadhyay, Anup Mondal and Pulakesh Bera, **RSC Adv.**, **2015**, **5**, 52235–52242.
- [4] A pyrazolyl-based thiolato single-source precursor for the selective synthesis of isotropic copper-deficient copper(I) sulfide nanocrystals: synthesis, optical and photocatalytic activity Gopinath Mondal, Ananyakumari Santra, Pradip Bera, Moumita Acharjya, Sumanta Jana, Dipankar Chattopadhyay, Anup Mondal, Sang Il Seok, Pulakesh Bera, **J Nanopart Res.**, **2016**, **18**, 311.
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- [6] New pyrazole based single precursor for the surfactantless synthesis of visible light responsive PbS nanocrystals: Synthesis, X-ray crystallography of ligand and photocatalytic activity, Ananyakumari Santra, Gopinath Mondal, Moumita Acharjya, Pradip Bera, Abhimanyu Jana, Sang Il Seok, Pulakesh Bera *Accepted manuscript, Nano Sc. and Nano Objects.*
- [7] *In vitro* evaluation of antibacterial, antifungal and larvicidal activities of pyrazole/pyridine based compounds and their nanocrystalline MS ( $\text{M}=\text{Cu}$  and  $\text{Cd}$ ) derivatives: Synthesis, X-ray crystallography and structure-activity relationship, Gopinath Mondal, Harekrishna Jana, Moumita Acharjya, Ananyakumari Santra, Pradip Bera, Abhimanyu Jana, Anangamohan Panja and Pulakesh Bera, *Medicinal Chemistry Review. Under review.*

