Executive Summary

of the UGC Major Research Project

(F.No.42-280/2013(SR) dated 12.3.2013)

"Design, development and characterization of mesoporous functional metal-organic framework (MOF)"

By Dr. Pulakesh Bera (Principal Investigator)

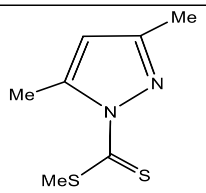
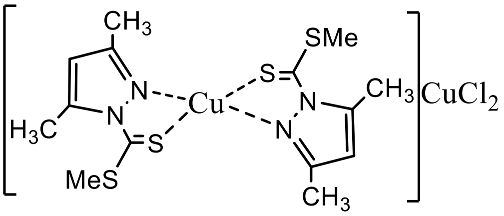
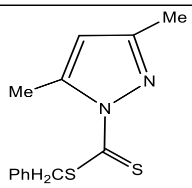
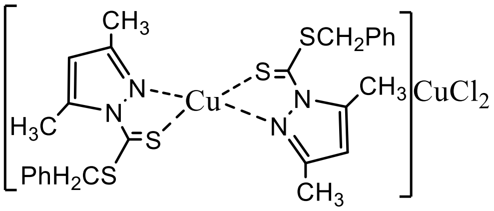
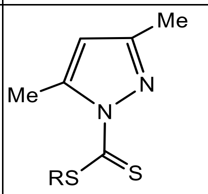
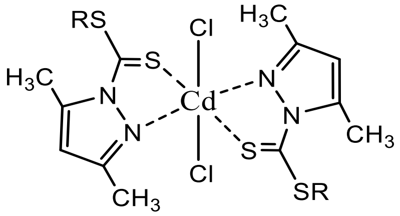
PANSKURA BANAMALI COLLEGE (Autonomous)

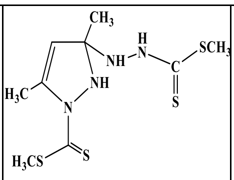
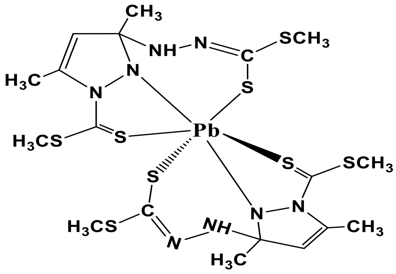
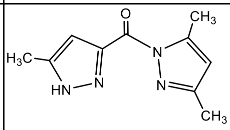
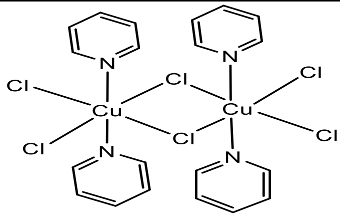
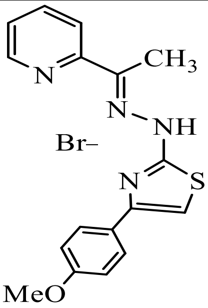
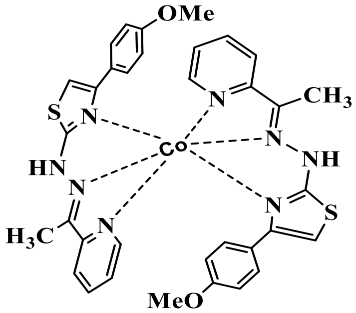
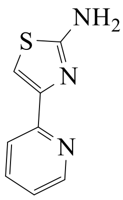
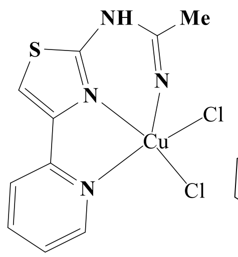
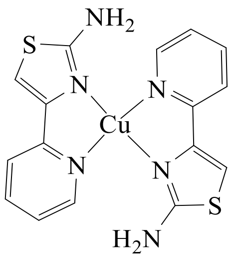
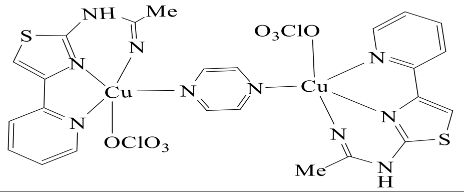
Affiliated to VIDYASAGAR UNIVERSITY, Midnapore – 721102

WEST BENGAL : INDIA

Summary: 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.	 (mdpa)	 $[Cu(mdpa)_2][CuCl_2]$	• Application in Cu_2S nanoparticles synthesis • Dye degradation study • Catechol oxidase mimetic activity • Thin films	[1] [1] [2] [3]
2.	 (bdpa)	 $[Cu(bdpa)_2][CuCl_2]$	• Application in Cu_xS (x=2 or 1.97) nanoparticles synthesis • Catechol oxidase mimetic activity	[4] [2]
3.	 R= Me; (mdpa) CH_2Ph; (bdpa)	 R=Me; $[Cd(mdpa)_2Cl_2]$ CH_2Ph; $[Cd(bdpa)_2Cl_2]$	• Application in CdS nanoparticles synthesis and photodegradation of Dye	[5]

4.	 (Hmdpc)	 [Pb(mdpc)$_2$]	• Application in PbS nanoparticles synthesis • Photocatalytic activity	[6]
5.		 [Cu(μ-Cl)$_2$(pyridine)$_2$]$_n$	• Antibacterial activity and anti-larval activity	[7]
6.	 (HL·Br)	 [CoL$_2$]ClO$_4$	• Antibacterial activity and anti-larval activity	Work in progress
7.		  	• DNA interaction study • Cell cytotoxicity • LDH study	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(mdpa)$_2$][CuCl$_2$] (sl. no. 1) derived from pyrazolyl dithiocarbazate ligand has been used to selectively synthesize hexagonal Cu_2S nanoparticles in a solvothermal process. The presence of the +1 oxidation state of copper is helpful for the selective synthesis of Cu_2S. The distorted shape, the tetrahedral complex of Cu(I) and the low decomposition temperature (100°C) facilitate the formation of flower-like hexagonal chalcocite (Cu_2S) nanostructures with sufficient porosity and crystallinity in solvothermal process. Furthermore, the Cu_2S 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 Cu_2S is found to be 80% [1]. Further the complexes $[Cu^I(mdpa)_2][Cu^ICl_2]$ (sl.no. 1) and $[Cu^I(L_2)_2][Cu^ICl_2]$ (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 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-Cu_2S thin films on a fluorine-doped tin oxide coated transparent conducting TCO (SnO_2:F) glass substrate is carried out by chronoamperometry and cyclic voltammetry (CV) using an ethanolic solution of $[Cu(mdpa)_2][CuCl_2]$. The appropriate potential at which the formation of stoichiometric p-Cu_2S thin films occurs was found to be 0.48 V. The mechanism of the selective deposition of the p-Cu_2S 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 chalcosite phase of copper sulfide with preferential orientation along the (110) plane. The I–V characteristic of the as deposited Cu_2S/TCO thin film shows a non-ohmic behavior suggesting the formation of a p–n heterojunction diode. The p-Cu_2S/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 ($Cu_{2-x}S$, x = 0.03, 0.2) nanocrystals are synthesized from [$Cu(bdpa)_2$][$CuCl_2$] (sl. no2) . The nucleation and growth of Cu2-xS (x = 0.03, 0.2) are effectively controlled by the SP and the solvent in the solvothermal decomposition process. During decomposition, fragment benzyl thiol ($PhCH_2SH$) 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 Cu1.97S nanoparticles (djurleite), whereas nonchelating hydrazine hydrate (HH) shows the tendency to furnish hexagonal platelets of copper-deficient Cu1.8S. 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., [$Cd(mdpa)_2Cl_2$] and [$Cd(bdpa)_2Cl_2$] 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, [$Cd(mdpa)_2Cl_2$], with the SCH_3 group in the structure always produced spherical CdS nanoparticles wherein the SP, [$Cd(bdpa)_2Cl_2$], with the SCH_2Ph 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, [$Pb(mdpc)_2$] (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_2, PbS-graphene-TiO_2 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_2S 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].

References (Published Paper in the project):

[1] Precursor-driven selective synthesis of hexagonal chalcocite (Cu_2S) 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-Cu_2S thin films on TCO (SnO_2: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.**

[5] A new pyrazolyl dithioate function in the precursor for the shape controlled growth of CdS nanocrystals: optical and photocatalytic activities, Gopinath Mondal, Moumita Acharjya, Ananyakumari Santra, Pradip Bera, Sumanta Jana, Nimai Chand Pramanik, Anup Mondal and Pulakesh Bera, **New J. Chem., 2015, 39, 9487-9496.**

[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, ***Nano Sc. and Nano Objects***., **2017, 10, 91-99**.

[7] *In vitro* evaluation of antibacterial, antifungal and larvicidal activities of pyrazole/pyridine based compounds and their nanocrystalline MS (M=Cu and 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, **Med. Chem. Res., 2017, 26, 3046-3056.**