SYNTHESIS, CHARACTERIZATION, APLICATION OF METAL ORGANIC FRAMEWORK OF ZINC

An MSc Dissertation report by:

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April 2022

SYNTHESIS, CHARACTERIZATION, APLICATION OF METAL ORGANIC FRAMEWORK OF ZINC

A DISSERTATION REPORT

Submitted in Partial Fulfillment
Of
The Degree of MSc (Inorganic Chemistry)

By
Ms. Samiksha M Chodankar

To the

School of Chemical Sciences
Goa University
Goa 403206
APRIL 2022

CERTIFICATE

This is to certify that the dissertation entitled ***" Synthesis, Characterization, Application of Metal Organic Framework of Zinc"*** is bonafide work carried out by Ms. Samiksha M Chodankar under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. Dr. Sunder N. Dhuri	Miss. SamikshaChodankar
Guiding Teacher	MSc. Student
Vice-Dean(Research) of School of Chemical Sciences	
Goa University	

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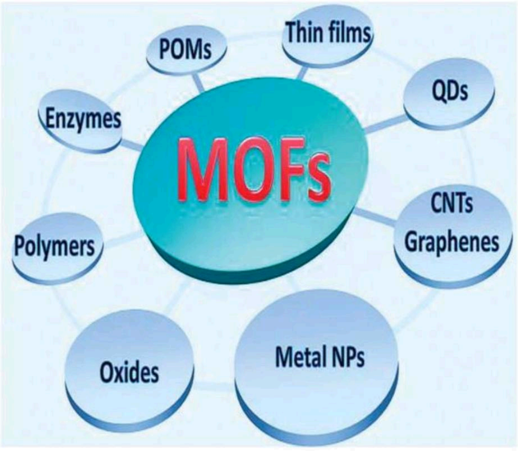
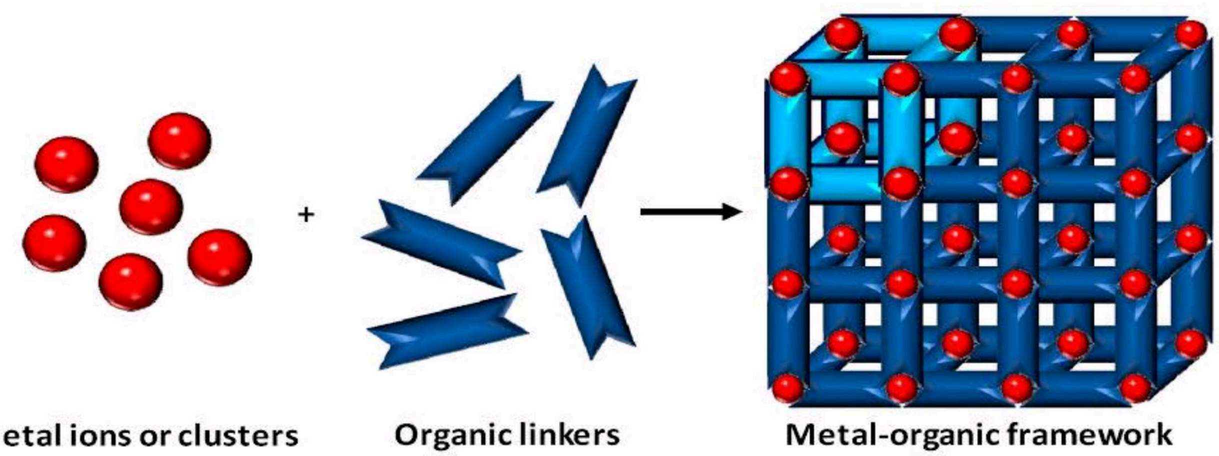
1)INTRODUCTION

Metal–organic frameworks (MOFs, which is also known as porous coordination polymers (coordination polymers (CPs) are hybrid organic-inorganic supramolecular structures self-assembled from metal nodes and/or metal clusters (metal particles smaller than 1nm) and organic ligands) PCPs) are an emerging class of highly engineered symmetric systems which can be built using metal nodes, organic spacers, and even solvent molecules by repeating the coordination frame in one, two, or three dimensions. Metalorganic frameworks (MOFs) are a subgroup of the CPs class, with tri dimensional crystalline regularity producing specific nano (<2 nm) or meso (2–50 nm) porous structures materials composed of inorganic clusters bridged by organic ligands constructed from metal containing nodes (also known as secondary building units, or SBUs) and organic linkers. MOF kind of structures were reported starting from 1960s by Tomic and others. Since the early 1990s, MOF research has been increased greatly especially with the rediscovery of MOF based porous materials by Yaghi and his research group. Omar Yaghi is a well-known pioneer and leader in developing the chemistry of metal-organic frameworks. He was recently ranked No. 2 among the world's top 100 chemists of the past decades (2000– 2010), based on the impact of his published research mostly in the field of MOFs and other porous materials. Their research group is noted for his contribution in introducing metal-oxide clusters as anchors for joining organic linkers into robust crystalline open frameworks with permanent porosity[1]. Their voids are functional cavities that can be selectively exploited. With proper choice of organic and inorganic components, the crystalline structure and chemical functionalities of MOFs on purpose can be modulated, which lead to their use in a wide range of applications. Because of their structural and functional tunability, the field of MOFs has become one of the fastest growing fields in chemistry which is demonstrated through the increase in number of structures, publications, and citations emerging, as well as by the constant expansion of research scope and researcher engagements[2].This unparalleled surge in MOF research can be ascribed to the following five developments: (1)advances in cluster chemistry,(2) maturation of organic synthesis pertinent to ligand preparation and post-synthetic modification,(3) improvement in structure determination, particularly through X-ray crystallography, and development of

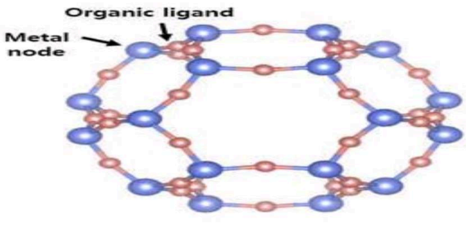


hard- and software for evaluation of sorption properties, (4) interdisciplinary growth of MOF research with its neighbouring fields, and (5) the ever-expanding potential in applications[3]. Since the 1990s, this area of chemistry has experienced an almost unparalleled growth, as evidenced by not only the sheer number of research papers published but also the ever-expanding scope of the research. The MOF field has recently been reviewed enormously. In 2009, the first themed issue of Chemical Society Reviews committed to MOFs was published and it has been a success, as evidenced by the record of a number of citations it has received. Additional themed issues and monographs focusing on this research area have also been published elsewhere.[4]As an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6000 m^2/g. These properties together with the extraordinary degree of variability for both the organic and inorganic components of their structures, make MOFs of interest for potential applications in clean energy, most significantly as storage media for gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs. Additional applications in membranes, thin film devices, catalysis, and biomedical imaging are increasingly gaining importance.[5]The high internal surface area and versatile architectures of MOFs make them promising candidates for development of advanced drug delivery systems, nitric oxide storage, imaging and sensing applications. Design and modification of organic ligands (i.e. carboxylates, imidazolates or phosphonates) connected strictly to metals (i.e. ions or clusters) led to development of MOFs with the highest tuneable porosities which is ideal for capture, storage, and/or development of practical/ efficient drug delivery systems, encapsulation of drugs, cosmetics, active gases imaging and effective theragnostic. MOFs can exhibit hydrophilic/hydrophobic entities, as well as the flexible structure which enables the adaptation of their porosity to the physicochemical features of each drug or gas. Based on the geometries of the organic linkers and coordination modes of the inorganic metal ions or clusters of metal ions, their structures can be designed according to targeted properties. A key structural feature of MOFs is the ultrahigh porosity (up to 90% free volume) and incredibly high internal surface areas, extending beyond a Langmuir surface area of 10000 $m^2\ g^{-1}$ which play a crucial role in functional applications, typically in storage and separation sensing, proton conduction and drug delivery. Generally porous MOFs show microporous characters (<2 nm) whereas the pore sizes could be tuned from several angstroms to several nanometres by typically controlling the length of the bi- or multipodal rigid organic linkers. In addition, versatile framework functionalities beyond their accessible porosity can arise from the metal components (e.g. magnetism, catalysis), organic linkers (e.g. luminescence, nonlinear optics

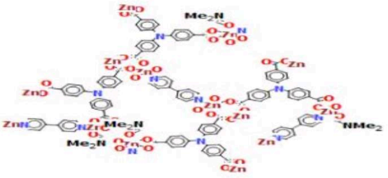
(NLO), chirality) or a combination of both. Nevertheless, MOFs exhibit a few weak points such as poor chemical stability that impede the use of their full potential. In order to satisfy the realistic applications of MOFs, it is desirable to further enhance the properties and introduce new functionalities. Fortunately, combining MOFs with a variety of functional materials has been proposed recently to combine the merits and mitigate the shortcomings of both the components. To date, MOF composites have been successfully made with active species, including metal nanoparticles/nanorods (NPs/NRs), oxides, quantum dots (QDs), polyoxometalates (POMs), polymers, graphene, carbon nanotubes (CNTs), biomolecules and so on, resulting in a performance unattainable by the individual constituents Moreover, they offer the great advantage of a flexible design, that it, one can tailor make the materials as per the specifications of optimum design.



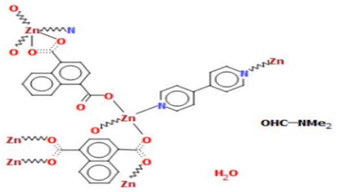
[2]Zinc (II) cation is an environmentally friendly metal, less expensive, easy to dispose of, and managed. Highly engineered symmetric systems can be built using zinc (II) atoms as the metal nodes of hybrid organic-inorganic supramolecular structures. Because of its unique photophysical properties, zinc (II) cation claims a role in designing novel chemo and biosensors, markers, and drug carriers. The non-toxic, abundant, and inexpensive zinc (II) metal cation offers several benefits in building versatile CPs structures, MOFs, and other NPs. The scale and the nature of cell and tissues is meaningful and imposes some structural, optical, and biological constraints that zinc ion can satisfy.[5]



2) LITERATURE REVIEW

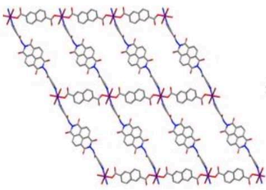


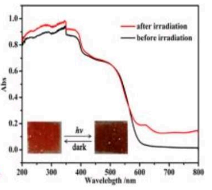
Guo-Gen Cui, Xiao-Xi Yang and Jian-Ping Yang synthesised a novel three-dimensional ZnII complex, poly [[(μ_2-4,4'- bipyridine) (μ_4-naphthalene-1,4-dicarboxylato) (μ_2-naphthalene- 1,4-dicarboxylato) dizinc(II)] dimethylformamide mono solvate monohydrate], (CCDC code: JUPLUD), $\{[Zn_2(C_{12}H_6O_4)_2(C_{10}H_8N_2)]\circ 2C_3H_7\text{-}NO\circ H_2O)\}n$ has been prepared by the solvothermal assembly of $Zn(NO_3)\circ 6H_2O$, naphthalene-1,4-dicarboxylic acid and 4,4'-bipyridine.[6]



A metal–organic framework with a novel topology, poly[sesqui(μ_2-4,4',4''-bipyridine) bis(dimethylformamide)bis(μ_2-4,4',4''-nitrilotribenzoato) tri zinc(II)], $[Zn_3(C_{21}H_{12}NO_6)_2(C_{10}H_8N_2)_{1.5}(C_3H_7NO)_2]_n$(CCDC no: VIYZIO01) was obtained by the solvothermal method using μ_2-4,4',4''-nitrilotribenzoic acid and 4,4'-bipyridine (bipy). The structure, determined by single-crystal X-ray diffraction analysis, possesses three kinds of crystallographically independent Zn(II) cations, as well as binuclear $Zn_2(COO)_4(bipy)_2$ paddle-wheel clusters, and can be reduced to a novel topology of a (3,3,6)-connected 3-nodal net, with the Schläfli symbol $\{5.6^2\}_4\{5^2.6\}_4\{5^8.8^7\}$ according to the topological analysis[7].

$[Zn(H_2O)_2(2,6\text{-NDC})(NDI\text{-A})]\cdot 2H_2O$ (NDI-A=naphthalene carbodiimide-based acceptor, 2,6-NDC^{2-}=2,6 naphthalenedicarboxylic group) MOF was synthesised by Man-Lu Wang, Chen Fu, Li Li, Hong Zhangwhich which showed excellent thermal stability proved by thermogravimetric analysis (TGA). The structure is stable from room temperature to 380°C.On irradiation by 300W xenon lamp compound showed photochromic and photo-controlled fluorescence quenching phenomenon with the formation of NDI-A radicals originated from electron transfer process which is based on both NeH···O hydrogen bond and π-π stacking interactions, which is not exhibited for NDI-type photochromic MOFs. The compound was further characterised by UV–visible absorption spectroscopy showed a strong broad absorption band in the range of 200–400 nm, which relates to n–π* and π–π* transition of the aromatic organic ligands, electron paramagnetic resonance spectroscopy (ESR) and fluorescent spectroscopy. The Powder X-ray diffraction (PXRD) of the crystalline material shows that experimental, after

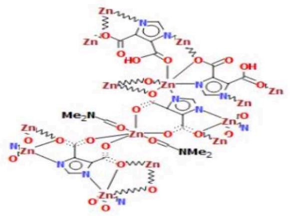




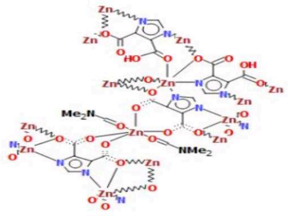
irradiation and decoloured absorption peaks all match well with simulated PXRD, which suggests the favourable phase purity of compound.[8]

In this paper, Ling Xu,Eun-Young Choi ,Young-Uk Kwon prepared an IL, 1-ethyl-3-methylimidazolium bromide ([EMI]Br) (white solid, M.P. = 80–82^{0}C, Yield: 92%) according to the literature method and used it as a solvent for synthesising a 3D $[Zn_4(BTC)_2(\mu_4$-$(H_2O)_2]$MOF by ionothermal synthesis with distorted tetranuclear $[Zn(\mu_4$-$O)]$ subunits employing $Zn(NO_3)_2{\circ}6H_2O$ and H_3BTC ligand (H_3BTC=1,3,5-benzenetricarboxylicacid).The compound features a 3-D architecture constructed by linking $[Zn(\mu_4$-$O)]$ subunits with BTC^{3-} ligands. They are composed of two five-coordinated and two four-coordinated Zn ions, different from the units of other MOFs. The experimental XRPD pattern for the compound matches well with the one simulated from single crystal structure data which indicated that the compound was isolated as a single phase.TG data of the compound shows that it has high thermal stability and the skeleton of the framework begins to decompose at 358^{0}C. FT-IR spectrum showed asymmetric stretching vibration $\nu_{as}(COO^-)$ which was observed at 1628 cm^{-1} and the symmetric stretching vibration $\nu_s(COO^-)$ at 1383 cm^{-1}. These peaks were shifted to lower values compared with the carbonyl frequencies of free H_3BTC ligand. The difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ was 245 cm^{-1}, characteristic for coordinated carboxylate groups. The peaks from 2886 to 2970 cm^{-1}were from C–H stretching vibrations.[9]

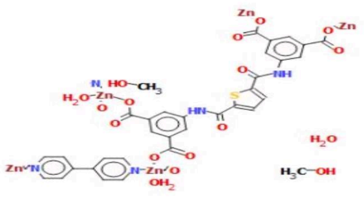
Mohammad Yaser Masoomi, Minoo Bagheri, Ali Morsali prepared by sonochemical process a 3D porous Zn(II)-based metal-organic frameworks $[Zn(oba)(4\text{-}bpdh)_{0.5}]_n\cdot(DMF)_{1.5}$(TMU-5) and $[Zn(oba)(4\text{-}bpmb)_{0.5}]_n$ $(DMF)_{1.5}$(TMU-6) micro, nanorods and plates .This were synthesized by ultrasonic irradiation using a non-linear dicarboxylate (H_2oba = 4,4-oxybisbenzoic acid) and two linear N-donor (4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene and 4-bpmb = N^1·N^4-bis((pyridin-4-yl)methylene)benzene-1,4-diamine) ligands Various sonication time and concentrations of initial reagents were evaluated to prepare the nanostructure of these MOFs. The morphology and size of TMU-5 and TMU-6 were investigated using scanning electron microscopy (SEM) by changing two parameters; sonication time and concentration of starting materials as well as control of nucleation. The best uniform distribution of nanorods and plates of TMU-5 and TMU-6 were obtained in lower concentrations of initial reagents, while, by increasing the rate of nucleation, sizes of the obtained MOFs were reduced. These results show that sonochemical process is an effective method for fast and simple preparation of nano-MOFs. The IR spectra of both crystals and nanorods of TMU-5 and TMU-6 produced by conventional heating and sonochemical method show the symmetric $\upsilon_{sym}(COO^-)$ and asymmetric $\upsilon_{asym}(COO^-)$ vibrations of the carboxylate groups around 1400 cm^{-1} and 1600 cm^{-1}, respectively. Also the characteristic absorption peak (C=O = 1679 cm^{-1}) of DMF is observed in IR spectra of these two MOFs.Calcination of TMU-5 and TMU-6 at 550°C under air atmosphere yields ZnO (ZnO is a n-type semiconductor material with a wide band gap energy of 3.37eV, and has potential applications as a material including solar cells, luminescent materials, transparent conductors and gas sensors)nanoparticles.Bragg diffraction peaks exhibit the typical patterns of hexagonal wurtzite structure of ZnO consistent with the reported data by the JCPDS card number 361451 with lattice parameters of a = 3.25 Å and c = 5.20 Å. These nano-MOFs were used as adsorbents in rhodamine B dye (RhB) adsorption (TMU-5 and TMU-6 exhibited maximum percent adsorption of 96.2 and 92.8 % of 100 ppm rhodamine B dye, which obeyed first order reaction model were fitted with the experimental data with good correlation coefficients. Their findings may provide some insight into preparation of high performance adsorbents with practical applications in RhB removal.[10]



Rui-Qin Zhong,Ru-Qiang Zou, Qiang Xu solvothermal synthesized Microporous zinc(II) imidazole-4,5-dicarboxylate, $[Zn_5(L)_2(HL)_2(DMF)_4]_n$ (H_3L = 4,5-imidazoledicarboxylic acid) (CCDC code: 600422) MOF, structurally characterized by single-crystal X-ray diffraction. Thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) experiments were conducted to determine the thermal stability.The compound after guest exchange shows high crystallinity as indicated by sharp peaks observed in the PXRD pattern. This compound crystallizes in the orthorhombic system with the space group Pbca and cell parameters a =14.1613A˚, b = 15.6764A˚, c = 16.1345 A˚, V = 3581.8A˚ and Z = 4. The crystal structure presents a 3D framework with the rare four-fold helical structure and open channels, which exhibited guest-coordination sites at channel walls and strong fluorescent emission. The strong blue emission in the solid state can work out as a material for blue-light-emitting diode devices.[11]

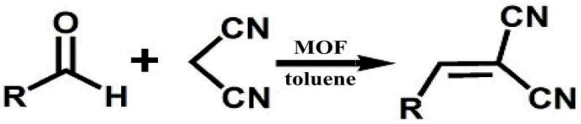


A multi-functional metal-organic framework (MOF) with the formula $[Zn_2(L)(4,4'\text{-}bpy)(CH_3OH)(H_2O)_2]\cdot 3.5H_2O\cdot CH_3OH$(MOF1) ($H_4L$ = 2,5-bis-(3,5 dicarboxyphenyl)thiopheneamide,4,4′-bpy = 4,4′-bipyridine) catena-[(μ-4,4'-bipyridine)-(μ-5,5'-[thiene-2,5-diylbis(carbonylazanediyl)]di(benzene-1,3-dicarboxylato))-diaqua-(methanol)-di-zinc methanol solvate hydrate(CCDC code AWEJOE) has been successfully synthesized under solvothermal condition by Fengqin Wang, Keheng Xu, Zheng Jiang, and characterized by single crystal X-ray diffraction analysis showed MOF1 crystallizes in triclinic space group $P\bar{1}$ and has a 2D layer framework. In addition, the phase purity of MOF1 was confirmed by the comparison of the simulated PXRD pattern from the crystal data with the experimental one The TGA curve of MOF1 exhibits a weight loss of 9.58% from 24 and 148 °C The coordinated water molecules are removed at the temperature between 148 and 279 °C, showing a weight loss of 4.14% (calc: 3.82%). Then, with the temperature increasing above 333 °C, the framework completely decomposed. This material exhibits strong fluorescent emission in the solid state and ethanol suspension at room temperature. Therefore, it is chosen as fluorescence probe for sensing aromatic amines and metal ions. The results reveal that MOF1has dual-functional sensing performance, which can sense anilines and Al^{3+} as well Fe^{3+} ions selectively and reversibly through fluorescence enhancement or quenching effect.MOF1 (120 mg) was dispersed in $Fe(NO_3)_3\cdot 6H_2O$ aqueous solution (15 mL, 0.01 M) at room temperature. After which the mixture was stirred for 24 h, the Fe^{3+}@MOF1 composite material was centrifuged and rinsed with water, and finally dried at 60 °C for 24 h in an oven. Fe^{+3}@MOF1 composite material was characterized by PXRD, IR and XPS. The XPS results show that 4.87% of Fe^{3+} ions were doped into MOF1, substituting part of Zn^{+2} ions in the framework. Moreover, the framework of Fe^{3+}@MOF1 was still well retained after doping by IR and PXRD spectra. In addition, the photocatalysis activities of MOF1 and Fe^{3+} doped composite material (named Fe^{3+}@MOF1) for degradation of Rhodamine B (RhB) were also studied. The experiment results show that Fe^{3+}@MOF1 has the improved photocatalytic activity than MOF1, suggesting that doping Fe^{3+} ions into the framework of MOFs would be an ideal option for enhancing their photocatalytic activities. Based on the excellent fluorescence emission the fluorescence titration, anti-interference and cyclic experiments of MOF1 were conducted in detecting of aromatic amines and metal ions. The experiment results demonstrated that the fluorescence intensities of MOF1 can be effectively quenched in the presence of p-



nitroaniline as well as Al^{3+} and Fe^{3+} ions with high sensitivity, selectivity, and quick regeneration. For diphenylamine, a new emission peak appeared along with the original emission quenching. This work confirmed that MOF1 could be used as an efficient fluorescence sensor for differentiating aromatic amines and metal ions. In addition, we also studied the photocatalytic activities of MOF1 and Fe^{3+}@MOF1 composite material. The results suggest that the introduction of Fe^{3+} ions can improve photocatalytic activities of MOF1. All these facts indicate that MOF1 can potentially be applied not only as an efficient luminescent sensor for aromatic amines and metal ions detection but also as a promising material for degradation of organic dyes, which contributed in detecting and treating environment pollutants.[12]

Recently, many efforts have been focused on the development of MOFs as heterogeneous catalysis. In this communication, Shixing Zhang, Hongming He, Fuxing Sun, Nian Zhao, Jianshi Du, Qinhe Pan, Guangshan Zhu selected adenine (ad)(Adenine, as an aromatic N-heterocycles, not only has lots of nitrogen atoms to coordinate with metal ions, but also contains amino groups as Lewis basic sites) and tetracarboxylic acid, namely 5,5'-(1,3,6,8-tetraoxobenzo[Imn][3,8]phenanthroline-2,7-diyl)bis-1,3-benzenedicarboxylic acid (H4L), as organic linkers to assemble with Zn(II) ions to construct a novel adenine-based porous $[H_2N(CH_3)_2]$•$[Zn_4(L)_{1.5}(ad)_3(H_2O)_2]$•4DMF MOF (denoted as JUC-188, DMF = *N*, *N*-dimethylformamide). The yellow crystals of JUC-188 were successfully obtained *via* heating these organic ligands and $Zn(NO_3)_2$•$6H_2O$ in a mixture of DMF and H_2O at 135 °C after 3 days. There are three different inorganic clusters in the framework, including ZnO_2N_2, $Zn_2O_2N_6$, and ZnO_5N clusters. From the single-crystal X-ray diffraction analysis, it exhibits that JUC-188 crystallizes in the triclinic space group P-1 and the asymmetric unit contains four Zn(II) ions, one and a half L^{4-} organic ligands, three adenine ligands and two terminal coordinated water molecules. There are three different Zn(II) clusters in the structure. From the thermogravimetric analyses (TGA) results, the as-synthesized JUC-188 showed a gradual weight loss before 200 °C about 19.78%, corresponding to the loss of one [H2N(CH3)2] cation, two coordinated water and four DMF guest molecules (calculated 19.44%) The main framework of JUC-188 began to collapse with the increasing of heating temperature. the characteristic peaks of adenine and H_4L ligands were both found in the FT-IR spectrum of JUC-188, which undoubtedly exhibited that both organic ligands coexisted in JUC 188.Interesting, the resultant porous MOF, namely $[H_2N(CH_3)_2]$•$[Zn_4(L)_{1.5}(ad)_3(H_2O)_2]$ •4DMF, retains free amino groups in the framework, which can be served as Lewis basic sites to catalyse Knoevenagel condensation reaction. Which was studied, the catalytic properties of JUC-188 for the basic catalytic Knoevenagel condensation, is mainly ascribed to the free amino groups in JUC-188.

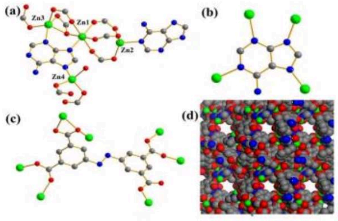


The results demonstrated that JUC-188 can effectively catalyse small aldehydes as substrates into their corresponding products. The catalytic efficiency depends on the molecule interactions between the substrate and the catalytic sites. The catalytic study exhibits that the as-synthesized MOF with free amino groups can be used as heterogeneous catalysis with remarkable catalytic efforts and good recycle.[13]

Entry	R	Time (h)	**Yield (%)**
1	*Ph*	3	97
2	*4-MePh*	3	95
3	4-NO_2Ph	2.5	97
4	*4-FPh*	2.5	98
5	*4-OMePh*	2.5	97
6	*1-naphthyl*	6	43
7	*anthryl*	6	21

Knoevenagel condensation of different substrates with malononitrile in the presence of JUC-188 as a solid catalyst.

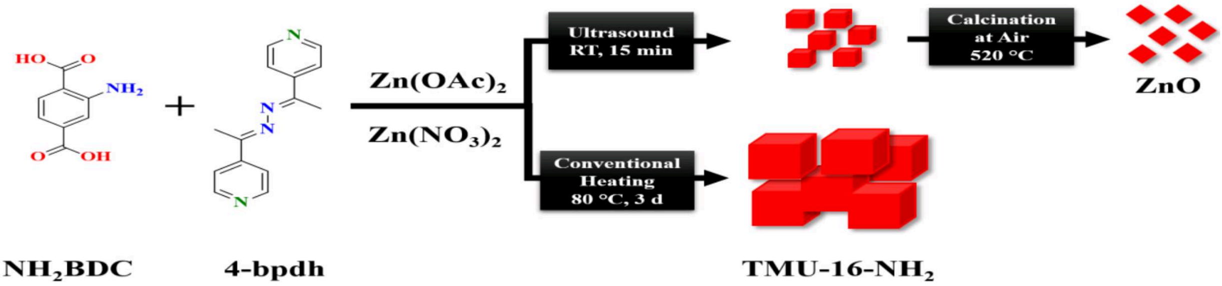
Herein, Jie Du, Guanglong Zou used a four-carboxylic acids linker, namely 3, 3', 5,5'-azobenzene-tetracarboxylic acid (H_4abtc), and adenine (ad) as the organic building blocks to form a novel microporous zinc(II) metal-organic framework with highly selective adsorption of CO_2 over CH_4. MOFs not only because they are suitable to construct microporous frameworks, but also exhibit multi-connectivity abilities. A microporous zinc(II) MOF material, $[H_2N(CH3)_2]$•$[Zn_4(abtc)_2(ad)H_2O)]$•4DMF was successfully synthesized under solvothermal reactions. The resulting material demonstrates high selectivity towards CO_2 uptake over CH_4. The ligands can be successfully assembled with Zn(II) ions to form an unprecedented microporous MOF based on $Zn_3(COO)_6N_3$ and $Zn(COO)_2N$ as secondary building units (SBUs), namely $[H_2N(CH_3)_2]$•$[Zn_4(abtc)_2(ad)H_2O)]$•4DMF (hereafter denoted as complex 1, DMF = N, N-dimethylformamide). Complex was successfully synthesized by heating such ligands and $Zn(NO_3)_2$•$6H_2O$ in a mixed solvent of DMF and water for three days at 135^{0}C. A single-crystal X-ray diffraction analysis reveals that complex crystallizes in the monoclinic space group $P_{2(1)}$/c and shows a 3D coordination framework. Powder X-ray diffraction (PXRD) pattern confirmed the phase purity of the as-synthesized sample. The thermogravimetric



analyses (TGA) of complex 1 exhibited a slow weight loss of 25.08% before 200 °C, which corresponds to the loss of one $[H_2N(CH_3)_2]$ cation and four DMF guest molecules (calculated 24.44%). The framework started to collapse with the increase of temperature. From the FT-IR spectra, the characteristic bands for both adenine ligands (1440 and 1153 cm^{-1}) and H_4abtc (772 and 666 cm^{-1}) in complex were observed, which undoubtedly indicated that both components existed in complex. The sorption behaviours of the activated sample for CO_2 and CH_4 at different temperatures was performed. the CO_2 uptake values are 39.22 cc g^{-1} (1.75 mmol g^{-1}) at 1atm and 273 K, and 27.50 cc g^{-1} (1.23 mmol g^{-1}) at 1atm and 298 K, respectively, while the CH_4 uptake amounts are 6.63 cc g^{-1} (0.30 mmol g^{-1}) at 1atm and 273 K, and 3.45 cc g^{-1} (0.15 mmol g^{-1}) at 1atm and 298 K. The adsorption isotherms at 273 and 298 K using the virial method was done, the Q_{st} value of complex for CO_2 is higher than those of many MOFs mainly due to the strong interactions between CO_2 and the microporous framework with exposed Zn(II) sites with the nitrogen atoms and $-NH_2$ groups.[14]

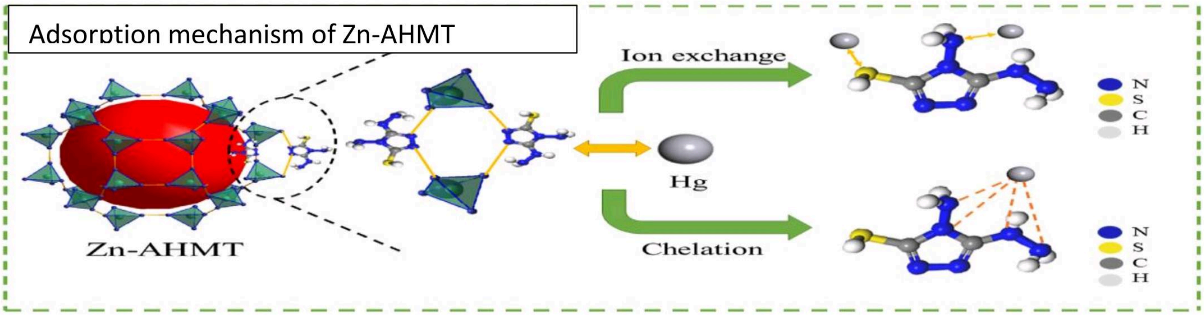
In this work, Prashant Mishra a, Samuel Mekala, Freider Dreisbach , Bishnupada Mandal , Sasidhar Gummaa,studied the adsorption characteristics of four industrially relevant gases (CO_2, CH_4, CO and N_2) on ($Zn_2(bdc)_2(dabco)(H_2O)_{0.5}(DMF)4$) ZnDABCO metal organic framework. Three weight loss steps were observed in thermo-gravimetric analysis. The N_2 physisorption isotherm at 77 K was used in calculation of surface area and pore volume of the sample. The adsorption isotherms measured at three different temperatures to enable us to model and calculate adsorption enthalpy from the experimental data. As expected the adsorption enthalpy at zero coverage was highest for CO_2. The adsorption capacities follow the order $CO_2 > CH_4 > CO > N_2$.The capacity and enthalpy of adsorption were compared with available literature data for a variety of adsorbents. The enthalpy of adsorption and Henry constants were lower than that on MOFs containing open metal centres like CuBTC and MIL-101 and should make ZnDABCO attractive for a separation process, as it would require milder regeneration conditions. The selectivity's at the zero-pressure limit for CO_2/CO, CO_2/CH_4 and CO_2/N_2 mixtures are 6.8, 3.3 and 8.4 respectively. The Ideal Adsorbed Solution Theory (IAST) also predicts enhancement in selectivity with pressure and CO_2 mole-fraction. ZnDABCO showed selectivity >2 for CH_4. This can be readily attributed to absence of open metal centers in the framework.[15]

Vahid Safarifard, Ali Morsali gave us the Facile Preparation of Nanocubes Zinc-based Metal-organic Framework by an Ultrasound-assisted Synthesis Method which can act as a precursor for the Fabrication of zinc oxide octahedral nanostructures. The synthesis of metal-organic framework (MOF) materials via ultrasound (US) irradiation involves shorter reaction times and offers enhanced control of particle size and morphology compared to conventional electric (CE) heating. Nanocubes of an interpenetrated pillared-layer Zn(II) metalorganic framework, $[Zn_2(NH_2\text{-}BDC)_2(4\text{-bpdh})]\cdot 3DMF$ (TMU-16-NH_2) (NH_2-BDC = amino-1,4-benzenedicarboxylate, 4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene, DMF = N,Ndimethylformamide), have been synthesized by US process and characterized by Field Emission Scanning Electron Microscopy (FE-SEM), powder X-ray diffraction, thermogravimetric analysis (TGA), elemental analysis and FTIR spectroscopy. The role of initial reagent concentrations and power levels of US irradiation and also reaction time, on size and morphology of nanostructure TMU-16-NH_2(Solvothermal synthesis of TMU-16-NH_2 was carried by $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1 mmol), 4-bpdh (0.119 g, 0.5 mmol), NH_2BDC (0.181 g, 1 mmol) which were dissolved in 15 ml DMF. The mixture was placed in a Teflon reactor and heated at 80°C for 3 days, and then it was gradually cooled to room temperature) have been studied. To prepare nano-sized S-TMU-16-NH_2, 25 ml solution of zinc(II) acetate dehydrate (0.5 mmol, 0.11 g; 0.02 M) in DMF was positioned in a high-density ultrasonic probe at ambient temperature and atmospheric pressure, operating with a power output of 12W. Into this solution 0.5 mmol (0.091 g) and 0.25 mmol (0.06 g) of the ligands $H_2BDC\text{-}NH_2$ and 4-bpdh, respectively, were added and sonicated for 15 min. The obtained precipitates were filtered off, washed with DMF and then dried in air, m.p. > 300°C. Moreover, ZnO octahedral nanoparticles were simply prepared through direct pyrolysis of the TMU-16-NH_2 nanocubes as a precursor at 520 °C without any surfactant or capping molecules.[16]



Here, Biao Zeng , Wei Wang, Sijin He , Guo Lin, Wenjia Du, Jun Chang , Zhao Ding synthesized the adsorbent (Zn-AHMT) from zinc nitrate and 4-amino-3-hydrazine-5-mercapto-1,2, 4-triazole (AHMT) by one-step method and characterized the microstructure and absorption performance by fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Thermal Gravimetric Analyzer (TGA) and X-ray photoelectron spectroscopy (XPS). Through a plethora of measurements, batch experiment results showed that the adsorption capacity of Zn-AHMT could reach 802.8 mg/g under the optimal pH 3 which proved that pH was a vital and essential factor affecting the removal efficiency of Zn-AHMT. Isothermal and kinetic experiments have confirmed that the reaction process of Zn-AHMT was chemisorption in accordance with Hill model and pseudo-second order model.

Adsorption mechanism of Zn-AHMT

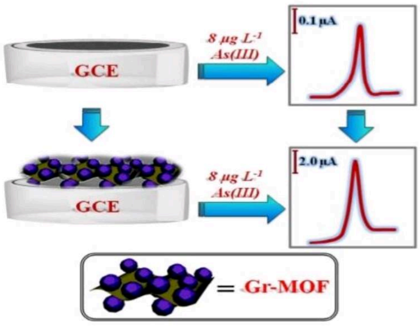


Thermodynamic experiments showed that the adsorption process was spontaneous and exothermic. Selectivity and repeated experiment indicated that the adsorbent had a stronger affinity for mercury ions than other ions, and the removal rate was above 98% each time. The adsorption mechanism had been studied by XPS, DFT calculations, frontier molecular orbital theory and showed that the adsorption process was mainly caused by the chelation and ion exchange between Zn-AHMT and mercury ions. The adsorption reaction was the result of the synergistic action of S and N atoms, and the product with Hg-N bond was more stable than that of Hg-S during adsorption. It could be seen that Zn-AHMT had great potential to remove mercury ions. Mercury (Hg) ions can lead to a serious impact on the environment; therefore, it was necessary to find an effective method for absorbing these toxic Hg ions.[17]

New Zinc functionalized metal organic Framework for selective sensing of chromate ion. A modified metal organic framework has been prepared R. Minmini, Sanay Naha, Sivan Velmathi by the solvothermal process of 2- (4-carboxyphenyl)-1, 3-dioxoisoindoline-5-carboxylic acid with $Zn(OAc)_2.2H_2O$. The framework has a PtS- type net. The obtained porous material has been characterized by Xray diffraction, Scanning electron microscopy, UV–vis spectroscopy, FTIR spectroscopy and BET surface area analysis. The BET surfaces area was 757m2/g^{-1}. The synthesized MOF exhibits reasonably good fluorescence characteristics. The luminescent studies indicate that the obtained Zn-MOF could be an efficient material for selectively sensing anion especially CrO_4 $^{2-}$. The mechanism of sensing is also studied in detail. The Zn-MOF senses the anion without altering its structural integrity.

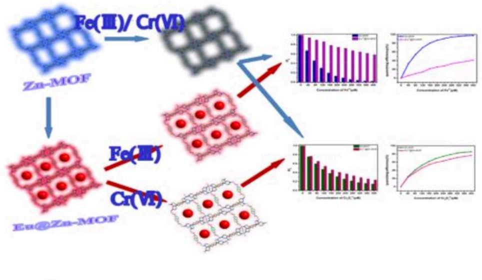
This post-synthesis route can be used for synthesis of isomorphous metal–organic frameworks that cannot be obtained by direct synthesis. In the present work, imide based organic linker molecule was synthesized in single step with good yield and the porous Zn-metal organic framework was successfully synthesized by solvothermal process. The powder X-ray diffraction (PXRD) patterns of as-synthesized are almost similar to the simulated from the literature depicts that the framework has been formed. And the shift in DR-UV spectroscopy also confirmed that the zinc had been coordinated with the organic linker. The highly ordered porous framework structure has been confirmed the SEM analysis. Further the formation of MOF is confirmed by the FTIR spectroscopy. The formed porous material was applied for sensing studies. The MOF successfully sense the chromate anion. The binding constant and effect of pH were also studied and found to be effective in biological pH range. The sensing property was also studied in detail. And further, the metal ion exchange studies were demonstrated to form Cu and Ni based MOF with good exchange ratio, which were difficult to prepare by direct synthesis method.[18]

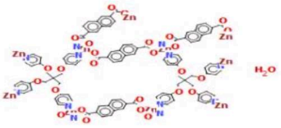
Application of graphene/zinc-based metal-organic framework nanocomposite for electrochemical sensing of As (III) in water resources. In this study, Mehdi Baghayeri, Masoud Ghanei-Motlagh, Reza Tayebee, Maryam Fayazi, Fatemeh Narenji prepared a novel nanocomposite of graphene oxide/zinc-based metal-organic framework (GO/MOF) through a simple solvothermal method. The electrochemical As (III) sensing capability of the nanocomposite was explored by casting the GO/MOF on a glassy carbon electrode (GCE), followed by an electrochemically reduction of GO. As(III) detection was performed by the differential pulse anodic stripping voltammetry (DPASV) method after closed-circuit mode. The present sensor showed excellent electrochemical performance such as a wide linear range from 0.2 to 25 ppb (µg/L), low detection limit (S/N=3) of 0.06 ppb and good reproducibility with a relative standard deviation (RSD) value of 2.1%. The detection limit of As(III) is lower than the threshold value set by the Environmental Protection Agency (EPA) in drinking water. A good selectivity for As(III) detection by the proposed Gr/MOF-GCE was also demonstrated. Finally, this platform was employed for the As(III) monitoring in environmental water samples, and the accuracy of obtained results were confirmed by inductively coupled plasma-optical emission spectrometer (ICP-OES) system.[19]



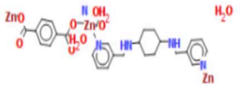
Amirhassan Amiri, Reza Tayebee, Abbas Abdar, Fatemeh Narenji Sani studied synthesis of a zinc-based metal-organic framework with histamine as an organic linker for the dispersive solid-phase extraction of organophosphorus pesticides in water and fruit juice samples. As a highly efficient adsorbent, the zinc-based metal-organic framework has been successfully synthesized from zinc as the metal ion and histamine as an organic linker under solvothermal conditions. The structure of nanocomposite was characterized by scanning electron microscopy (SEM), X-ray diffraction(XRD), and Fourier transform infrared (FTIR) analysis. The synthesized sorbent was applied for dispersive solid-phase extraction (DSPE) of organophosphorus pesticides (OPPs) in fruit juice and water samples. The gas chromatography-flame ionization detector (GC-FID) was used as instrument detection. The main experimental factors affecting the extraction efficiency such as the desorption conditions, sorbent amount and extraction time were evaluated and optimized. Good linearity exhibited for all of the target analytes in the 0.1–100 ng mL^{-1}concentration range. The enrichment factors (EFs) ranged from 803 to 914. The limits of detection (LODs) for the established DSPE-GC-FID method were found to be 0.03–0.21 ng mL^{-1}.The DSPE-GC-FID method can be used for the analysis of OPPs in water and fruit juice samples with recoveries of the analytes in the range of 91.9% to 99.5%.[20]

A new luminescent Zn(II)-based metal−organic framework (MOF), $[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$ (Zn-MOF; TPOM =tetrakis(4-pyridyloxymethylene)methane and H_2ndc = 2,6-naphthalenedicarboxylic acid), was successfully synthesized by a hydrothermal reaction, this represents the first example of MOF-based luminescent sensors that can differentiate Fe(III) with Cr(VI) ions through the fluorescence mechanism. This work demonstrates the potential application of Zn-MOF for the selective detection and differentiation Fe(III) and Cr(VI) ions, and it also provides a new facile route to designing functional MOFs as fluorescent sensors. Zn-MOF was selected as a parent coordination compound to encapsulate Eu^{3+} cations to obtain a Eu^{3+} -incorporated sample (Eu^{3+}@Zn-MOF). Subsequently, we explored the potential application of Eu^{3+}@Zn-MOF as a probe for the selective sensing of Fe(III) and Cr(VI) ions, and it revealed that we could differentiate Fe(III) and Cr(VI) ions by the combination Zn-MOF and Eu^{3+}@Zn-MOF.[21]





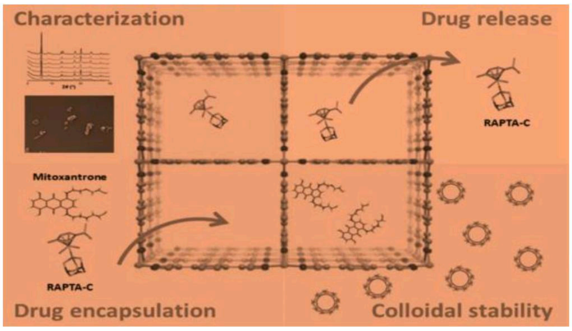
Yong-Ze Tzeng, Ching-Jung Chang, Ming-Chang Yang, Meng-Jung Tsai, Kentaro Teramura, Tsunehiro Tanaka, Hwei Voon Lee, Joon Ching Juan, Jing-Yun Wu, Yu-Chuan Lin gave Zn-Based Metal–Organic Frameworks which can be used as a sacrificial agent for the synthesis of Zn/ZSM-5 Catalysts and Their Applications in the Aromatization of Methanol. Zn/ZSM-5 catalyst made by using ZIF-8 as the sacrificial agent in steam-assist - crystallization (SAC) and hard templating Physicochemical characterization revealed that all Zn/ZSM-5 catalysts had finely dispersed Zn^{2+} species, i.e., ZnO and $Zn(OH)^+$. However, the concentration of Lewis acidic Zn^{2+} species and the compositions of $Zn(OH)^+$ and ZnO were different.CPO-1-Zn and ZIF-8 were the sacrificial agents in the synthesis of Zn/ZSM-5. ZIF-8 derived Zn/ZSM-5 had high concentrations of Lewis acidic Zn^{2+} and $Zn(OH)^+$. ZIF-8 derived Zn/ZSM-5 exhibited a higher activity in methanol aromatization.[22]



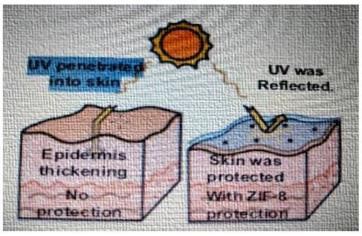
Manzar Sohail, Muhammad Altaf, Nadeem Baig, Rabia Jamil, Muhammad Sherc and Atif Fazald synthesised a new water stable zinc metal organic framework as an electrode material for hydrazine sensing. In this study, a new water stable Zn-MOF was synthesized and used directly as an electrode material. The Zn-MOF possesses good ability to electro catalyse the hydrazine oxidation reaction. The Zn-MOF's inherent poor conductivity was overcome by including a hydrophobic electrolyte, tetrakis(4-chlorophenyl)borate tetra dodecyl ammonium salt (ETH 500), during the fabrication of the Zn-MOF membrane. After coating a thin film of the nafion-ETH500 supported Zn-MOF over a glassy carbon electrode (GCE), the response for hydrazine oxidation was substantially improved. Linear sweep voltammetry (LSV) demonstrated a wide linear range from 20 to 350 mM ($R_2 = 0.9922$) for hydrazine. A detection limit of 2 mM (n = 3) was observed. The electrochemical behaviour of the ZnMOF/ETH500/nafion modified GCE revealed that MOFs have a promising future as electrode materials for direct electrochemical sensing. The results of this study demonstrate that the synthesis of MOFs can be tuned for their direct use as an electrochemical sensing platform. The ZnMOF/ETH500/nafion GCE demonstrated improved and stable electrochemical activity towards hydrazine. The ZnMOF conductivity on the electrode surface was improved with a well-known electrolyte, ETH500, in ISEs (ion-selective electrodes). The results revealed that the electrochemical behaviour of the GCE was considerably improved after coating with the ZnMOF/ETH500/nafion. This was evident from the shift of the hydrazine oxidation peak towards lower potential and the substantial improvement in the redox current with improved electrode kinetics of the ZnMOF/ETH500/nafion modified GCE. The wide linear range and the good limit of detection demonstrated that MOFs have a promising future in electrochemical sensing due to their unique and attractive structural features. However, a lot of further research is required to synthesize new MOFs with improved selectivity, redox capacity and electrocatalytic behaviour.[23]

Jian Shen, Nan Wang,Yang Guang Wang, Di Yu and Xiao–kun Ouyang for the first time, prepared a magnetic composite material by combining Fe_3O_4, MMT and Zn-BDC using a co-precipitation method and in situ polymerization. The influence of adsorption conditions on the adsorption capacity of MMMT@Zn-BDC for Pb(II) was examined, including the adsorbent dosage, pH of Pb(II) solution, initial concentration of Pb(II), and the temperature and adsorption time. Also, the adsorption mechanism was studied. The results of this study show that MMMT@Zn-BDC adsorbs Pb(II) via chemisorption. In addition, MMMT@Zn-BDC exhibits good potential for adsorbing Pb(II), including its high adsorption capacity (724.64 mg/g) and good recyclability. This magnetic compound was applied to adsorb Pb(II). Based on the results of adsorption isotherm and adsorption kinetics, the adsorption behaviour is in accordance with the Langmuir isotherm model and pseudo-second-order kinetics model, and the process of MMMT@Zn-BDC adsorbing Pb(II) is endothermic. The time required to reach adsorption equilibrium is 90 min. In addition, MMMT@Zn-BDC also exhibited excellent recycling performance.The removal rate remained at 80.45% after recycling five times. Its easy separation and sustainability make MMMT@Zn-BDC a superior adsorbent for removing Pb(II). The composite material MMMT@Zn-BDC was characterized by Zetasizer, SEM, TEM, FTIR, XRD, VSM, and XPS.[24]

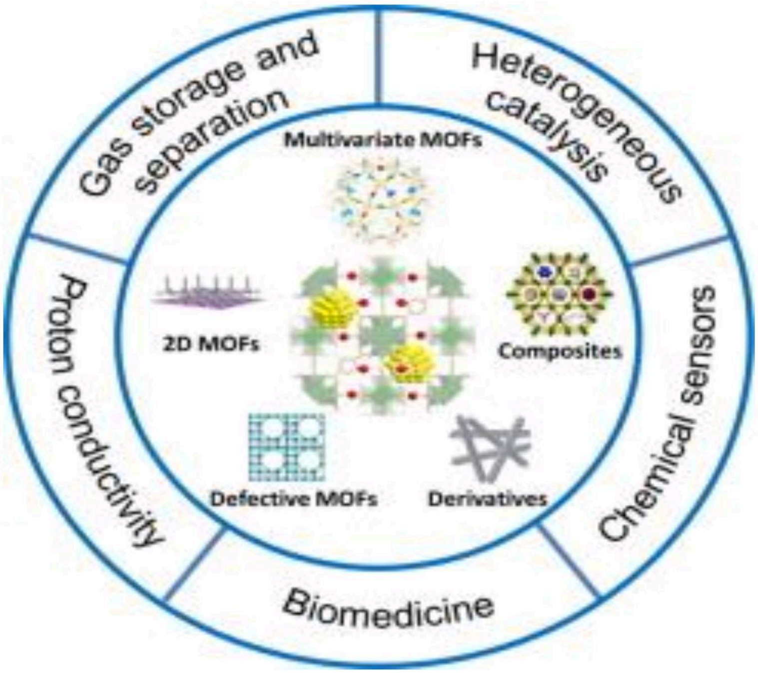
Sara Rojas, Francisco J. Carmona,Carmen R. Maldonado,Patricia Horcajada, Tania Hidalgo,Christian Serre,Jorge A. R. Navarro,and Elisa Barea work describes synthesis at the nanoscale of the isoreticular metal−organic framework (MOF) series ZnBDPX, based on the assembly of Zn(II) metal ions and the functionalized organic spacers 1,4-bis(1H-pyrazol-4-yl)-2-X-benzene (H_2BDP_X; X = H, NO_2, NH_2, OH). The colloidal stability of these systems was evaluated under different relevant intravenous and oral-simulated physiological conditions, showing that ZnBDPOH nanoparticles exhibit good structural and colloidal stability probably because of the formation of a protein corona on their surface that prevents their aggregation.Furthermore, two antitumor drugs (mitroxantrone and [Ru(p cymene) Cl_2(pta)] (RAPTA-C) where pta =1,3,5-triaza-7-phospaadamantane) were encapsulated within the pores of the ZnBDPX series in order to investigate the effect of the framework functionalization on the incorporation/delivery of bioactive molecules. Thus, the loading capacity of both drugs within the ZnBDPX series seems to directly depend on the surface area of the solids. Moreover, ligand functionalization significantly affects both the delivery kinetics and the total amount of released drug. In particular, ZnBDPOH and ZnBDPNH$_2$ matrixes show a slower rate of delivery and higher percentage of release than ZnBDPNO$_2$ and ZnBDPH systems. Additionally, RAPTA-C delivery from ZnBDPOH is accompanied by a concomitant and progressive matrix degradation due to the higher polarity of the BPDOH ligand, highlighting the impact of functionalization of the MOF cavities over the kinetics of delivery.[25]



Jisheng Xia, Haishan Li, Wanling Zha, Chengyuan Cai, Tingting You, Zhenyu Wang, Mengling Wang, Feng Zeng, Jinmei Cheng, Jiaxin Li and Xiaopin DuanHerein, herein choose four zinc-based MOFs with various bandgap energies were selected to investigate their optical behaviour's and evaluate their possibility as sunscreens. Zeolitic imidazolate framework-8 (ZIF-8) was found to possess the highest and widest UV reflectance, thereby protecting against sunburn and DNA damage on mouse skin and even achieving a comparable or higher anti-UV efficacy relative to the commercially available UV filters, TiO$_2$ or ZnO, on pig skin, a model that correlates well with human skin. Also, ZIF-8 exerted appealing characteristics for topical skin use with low radical production, low skin penetration, low toxicity, high transparency, and high stability.[26]



3) CONCLUSION



Here, we have summarized the main structural characters and recent functional applications of MOFs. The MOF field has undergone explosive growth especially in the past two decades, and the trend is continuing. While early applications of MOFs were focused on gas storage and separation due to their porous structures, more and more new applications such as catalysis, chemical sensors, proton conduction, and biomedicine are being developed. The structures of MOFs determine their functions, and the vast number of published MOF papers makes it possible to deduce structure–function relationships. For example, the gas storage and separation typically benefit from micropores, which match the sizes of particular gas molecules, while MOF composites and MOF catalysts often require meso- or macropores as well as open channels to facilitate mass transport. Compared to other traditional porous materials, MOFs have rich, highly ordered, and tunable structures. It is always fascinating to discover new MOF structures, but it suffices to say that the current emphasis of MOF research is on using structural information to either improve known functions or develop new functions of MOFs. MOFs can form composite materials with an endless list of other materials like metal nanoparticles, polymers, metal oxides, metal complexes, small organic molecules, and big biomolecules including enzymes and DNAs. The structures of MOFs can be finely tuned by direct or post-synthetic modification of the ligands, the metal SBUs, and inclusion of guest species. Despite the significant progress in an ever-increasing list of MOF-related research areas, a number of challenges remain. First, the exact MOF growth mechanism remains obscure. A precise control of the target structures for pristine MOFs remains difficult due to the limited understanding of self-assembly in a closed reaction system, for instance, the effect of synthetic condition on increasing or decreasing the surface area and pore size of MOFs.[27] Deep understanding of the self-assembly mechanism will allow us to design and construct suitable MOFs with regular or hierarchical pores, adjustable composition, and high surface area. Combining photochromic property with MOFs is a promising method to contain a new multifunctional material. As is well-known, varying the experiment condition can get different MOFs. Therefore, to select suitable photochromic organic ligands possess chemically modification ability is important considering factor to construct such photochromic MOFs.[9] Second, new strategies are still needed to construct MOF composite materials. It is always the goal of composite materials to synergistically combine the structural advantages of MOFs with the functions of the guest materials, but the experimental methods to achieve this are still limited. Third, the syntheses of many MOF-derived materials remain difficult to control. Despite the high surface area and high porosity of many MOF derived materials, precise control on the shape and size of their pores is often missing. Lastly, from the perspective of practical applications, issues including cost, stability, electrical conductivity, etc., of MOFs for industrially important reactions still need to be addressed.[27] Thus large-scale synthetic methods with high yield to afford low-cost MOFs are yet to be developed. Most practical applications of MOFs require high stability in the presence of moisture or water, but most MOFs have generally moderate to low stability in water. The stability of MOFs should be further improved under strongly acidic or basic conditions, despite the development of a number of MOFs with extremely high chemical and thermal stability. For electrocatalysis and related fields, most MOFs have shown poor electrical conductivity but many strategies have been developed to address the problem. For applications such as MOF-based catalysis, most studies have been focused on proof of concepts. More important industrially relevant reactions such as oil cracking and refinery, polymerization, and asymmetric synthesis of various chiral intermediates for pharmaceuticals need to be explored. In conclusion, MOFs have received tremendous advances from structural design and controllable synthesis to their functional applications in the past two decades. Although many obstacles remain to be solved on their way to the industrial applications, the academia and chemical industry are beginning to join hands to realize practical applications of MOFs. Herein, recent developments in the synthesis and post synthetic surface functionalization of MOF that strengthen the fundamental understanding of how such structures form and grow are highlighted; the internal structure and external surface properties of these various novel MOF are highlighted as well. These fundamental advances have resulted in MOF being used as integral part of research. [5] We expect a bright future for MOFs with the collaborative efforts from researchers in different fields including chemists, materials scientists, engineers, medical professionals, and others.[27]

4) ACKNOWLEDGEMENT

It was indeed a great sense of joy achieved to see this literature survey being completed. It has been a very faithful and enjoyable learning experience for me. The literature survey on which I have worked entitled Metal Organic Framework of Zinc was possible with constant guidance from our guide Dr. Sunder N Dhuri and his research students. I would to thank our guide for his constant supervision as well as for providing necessary information regarding the literature review. I would also like to thank School of Chemical Science’s Goa University for giving us excess to connectivity for downloading research papers. I would also like to thank our teachers Dr. Vinod Mandrekar ,Dr. Sandesh Bugde, Dr. Savita A Kundaikar for giving hand on training on various structure drawing software’s and use of Mandeley for citation and reference management. The fruit of this hard work comes from good guidance so I would also like to thank my classmates.

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