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A SHORT REVIEW ON SYNTHESIS AND APPLICATIONS OF ZINC BASED METAL ORGANIC FRAMEWORKS

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***Abstract*— Metal organic framework are a class of compounds consisting of metal ions or clusters that are coordinated to organic ligands to form one-, two, or three-dimensional structures. Zinc based metal-organic framework have great importance among a number of metal-organic framework, due to their utility for removal and detection of antibiotics in water, detection and differentiation of ferrous and chromium ions in aqueous solution, as an efficient catalyst, as photocatalyst, removal of emerging drug contaminant (amodiaquine) from aqueous solution, in drug delivery, cell imaging and sensing, as nontoxic and biodegradable platforms for biomedical applications, as an electrode material for hydrazine sensing and they also have many more applications.. All these characteristics have encouraged extensive study of the chemical, physical, biological and industrial properties of metal organic frameworks of zinc. So this review article provides a comprehensive overview of synthesis and most of the persists application of metal organic framework of zinc.**

***Keywords*— Zn-Metal organic framework, Application of Zn-Metal organic framework.**

I. INTRODUCTION

Nearly year of 2000, very small number of the MOFs were known and some of the materials with low porosity could be discussed as most of the MOFs known at that time would easily fit only in one chapter. From the year of 2016, after the progress of research work in the field of metal organic framework, recently [1-7] it is possible to create a very long list with MOF structures alone. This significant progress results in the discovery of materials with record large surface areas. At present, more than 10 000 MOFs are in existence.

Metal–organic frameworks (MOFs) are also proved as useful materials for environmental remediation due to their high surface area, porous structure, and application-specific tailoring of properties. In this regards, metal-organic frameworks based on transition metals are best catalysts and adsorbents for the remediation of gaseous and organic pollutants for the protection of our environment. A number of transition metal frameworks are known that are used to convert gaseous pollutants into important value-added compounds [8].

MOFs can be easily prepared by the simple combination of metal ions and organic bridging ligands possessing divergent donor atoms. This metal–ligand directed assembly approach can yield a new generation of multi-dimensional networks, which contain channels or cavities of various sizes and shapes [9-11]. Due to the porous features of such MOFs a wide range of applications can be envisioned namely in nonlinear optics [12, 13], gas storage [14-16], catalysis [17, 18] and host–guest induced separation [22-25]. Catalytic applications of such materials were among the earliest proposed ones [26], and nowadays many organic reactions can be efficiently catalyzed by MOFs [27-33].

A number of metal organic framework based on transition metals are available. Commonly used transition metals are iron, cobalt, nickel, zirconium, cadmium, copper, zinc, manganese, titanium and vanadium which are capable to link organic linkers and used for the synthesis of metal organic framework [34-36]. Among a large number of MOFs the authors selected zinc based metal-organic frameworks for their synthesis and applications in this review study due to their utility for removal and detection of antibiotics in water, for detection and differentiation of ferrous and chromium ions in aqueous solution, as an efficient catalyst, as photocatalyst, removal of emerging drug contaminant (amodiaquine) from aqueous solution, in drug delivery, cell imaging and sensing, as nontoxic and biodegradable platforms for biomedical applications, as an electrode material for hydrazine sensing..

II. SYNTHESIS AND APPLICATION

Shuang Gai et al were reported highly stable zinc-based metal–organic frameworks and some flexible composites for the removal and detection of antibiotics in water and they prepared two types of flexible three-dimensional (3D) zinc-based MOFs $\{[Zn_2\ (bcob)\ (OH)\ (H_2O)]\cdot DMA\}_n$ (ROD-Zn1) and $\{[Zn(\ Hbcob)]\cdot(solvent)\}_n$ (ROD-Zn2) (H_3bcob = 1,3-bis((4′-carboxylbenzyl)oxy)benzoic acid) with rod second

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building units (SBUs). They mainly observed that these MOFs possessed exceptional water and chemical stabilities (toward both acid and base), fast sorption kinetics and brilliant uptake capacity of various antibiotics in the aqueous environment. They also demonstrate that this adsorption activity was further optimized by preparing MOF-melamine foam (MF) hybrid composites, a hierarchical microporous–macroporous MOF @MF system (ROD-Zn1@MF and ROD-Zn2@MF), that can be recyclable after their adsorption activity and these MOFs exhibited good fluorescent properties. On the basis of these results they concluded that prepared ROD-Zn1 and ROD-Zn2 exhibited dual performance for detection and removal of antibiotics from water [37, 38].

Some zinc metal–organic framework for selective detection and differentiation of Fe(III) and Cr(VI) ions in aqueous solution were reported by Rui Lv et al [39, 40]. They synthesized a new type of luminescent Zn(II)-based (MOF), $[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$ (Zn-MOF; TPOM = tetrakis(4-pyridyloxymethylene)methane and H_2ndc = 2,6-naphthalenedicarboxylic acid) by a hydrothermal method. They observed that these MOF exhibits outstanding luminescence emission, and it can detect Fe (III) and Cr (VI) ions with high selectivity. They also observed that Fe(III) and Cr(VI) ions can be differentiate by the combination of Zn-MOF and Eu^{3+}@Zn-MOF. They concluded with the help of their observations that it represented the first example of MOF-based luminescent sensors which can detect and differentiate Fe(III) and Cr(VI) ions selectively.

Anirban Karmakar, M. Fátima, C. Guedes da Silva and Armando J. L. Pombeiro [41-42] were reported some zinc metal–organic frameworks which can be used as a efficient catalysts for the diastereoselective Henry reaction and transesterification. They studied three types of new MOFs by the coordination reactions of zinc(II) with compounds possessing different flexible side functional groups, 2-acetamidoterephthalic acid (H_2L1), 2-propionamidoterephthalic acid (H_2L2) and 2-benzamidoterephthalic acid (H_2L3) with the help of X-ray crystallography. They observed that the framework with the side functional groups of amidoterephthalic acid and/or auxiliary ligands was play significant roles. They demonstrated that these frameworks act as heterogeneous polymeric solid catalysts not only for the diastereoselective nitroaldol (Henry) reaction of different aldehydes with nitroalkanes but also for transesterification reactions. They concluded that these types of MOF-based heterogeneous catalysts can be recycled without losing their activity.

Fengqin Wang, et al [43], also reported a synthesis of multifunctional zinc-based metal-organic framework, $[Zn_2(L)(4,4'\text{-bpy})(CH_3OH)(H_2O)_2]\cdot 3.5H_2O\cdot CH_3OH$(MOF1) ($H_4L$ = 2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide,4,4′-bpy = 4,4′-bipyridine**)]** for sensing and photocatalytic applications by solvothermal method and characterize them by single crystal X-ray diffraction technique, IR spectroscopic technique, thermogravimetric analyses (TGA) and powder X-ray diffraction spectra. They found that this material exhibited strong fluorescent emission in the solid state and ethanol suspension at room temperature. They were also chosen it as fluorescence probe for sensing aromatic amines and metal ions. They observed that this **MOF1** has 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. They were also examines photocatalysis activities of **MOF1** and Fe^{3+} doped composite material (named **Fe^{3+}@MOF1**) for degradation of Rhodamine B (RhB) and they conclude on the basis of experiments that **Fe^{3+}@MOF1** has the improved photocatalytic activity than **MOF1** and suggested that doping Fe^{3+} ions into the framework of MOFs would be an ideal option for enhancing their photocatalytic activities.

A team of Adedibu C. Tella, Samson O. Owalude', Sunday J. Olatunji, Sunday E. Elaigwu, Lukman O. Alimi, Peter A. Ajibade, Oluwatobi S. Oluwafemi [44], reported the synthesis of zinc-carboxylate $[Zn_2(fum)_2(bpy)]$ and $[Zn_4O(bdc)_3]$ (fum = fumaric acid; bpy = 4,4-bipyridine; bdc = benzene-1,4-dicarboxylate) metal-organic frameworks as adsorbents, for the removal of emerging drug contaminant (amodiaquine) from aqueous solution. They were characterized these adsorbents by elemental analysis method, Fourier transform infrared spectroscopy and powder X-ray diffraction technique. They found that the adsorption process for both adsorbents follow the pseudo-first-order kinetics and the data of adsorption equilibrium follow the Freundlich isotherm. They also observed that maximum adsorption capacities for amodiaquine were found to be 0.478 and 47.62 mg/g on the $[Zn_2(fum)_2(bpy)]$ and $[Zn_4O(bdc)_3]$ MOFs respectively which were obtained at pH of 4.3 for both adsorbents. They also detect the presence of the drug in the MOFs after the adsorption process with the help of FT-IR. They concluded on the basis of these results that the prepared MOFs could be used for the removal of amodiaquine from wastewater

Rashda Safdar Ali, Hongmin Meng and Zhaohui Li [45], also reported some zinc-based metal-organic frameworks in drug delivery, cell imaging and sensing on the basis of the fact that zinc is a low-toxic transition metal cation, zinc-based MOFs used as drug carriers in the biological system [46], used in dermatology as a skin moisturizing agent with astringent, antibacterial agent and it has anti-inflammatory properties [47, 48]. They suggested that Zn-metal centres in MOFs have been created by improving drug delivery and these Zn-based MOFs have been appeared to be safe as it was elucidated by different cytotoxicity assays for targeted drug delivery. They also revealed that the MOF-based heterogeneous catalyst is durable and can regenerate multiple times without losing activity. They concluded that as a functional carrier for drug delivery, cell imaging, and chemosensory, the chemical composition and flexible porous structure of MOFs can be allowed to improve their medical formulation and functionality

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Sonia Bahrani, Seyyed Alireza Hashemi, Seyyed Mojtaba Mousavi and Rouhollah Azhdari [49] also reported a review study on zinc-based metal-organic frameworks as nontoxic and biodegradable platforms for biomedical applications and they also provide the literatures for addressing the biomedical applications of zinc-based MOFs to present recent achievements in this interesting field

Gajendra Gupta et al [50], reported the synthesis of a zinc-based MOF, AnDBP MOF, which was derived from anthracenedicarboxylic ligand and dipyridyl boron dipyrromethene (BODIPY) chromophore. They observed that the single-crystal structure of AnDBP MOF possess a no interpenetrate network structure with zinc metal binding the ligands in an octahedral fashion. They also revealed that this AnBDP MOF displayed an efficient energy transfer between the linkers and excellent photocatalytic properties.

A research team of Manzar Sohail, Muhammad Altaf, Nadeem Baig, Rabia Jamil, Muhammad Sherc and Atif Fazald [51], synthesized a different type of water stable zinc metal organic framework as an electrode material for hydrazine sensing. They observed that this Zn-MOF possesses good ability to electro catalyse the hydrazine oxidation reaction and inherent poor conductivity of the Zn-MOF was overcome by including a hydrophobic electrolyte, tetrakis(4-chlorophenyl)borate tetradodecylammonium salt (ETH 500), during the fabrication of the Zn-MOF membrane. They also observed that after coating a thin film of the nafion-ETH500 supported Zn-MOF over a glassy carbon electrode (GCE), the response for hydrazine oxidation was significantly improved. They concluded with the help of the obtained results and electrochemical behaviour of the ZnMOF/ETH500/nafion modified GCE that these MOFs can have a promising future as electrode materials for direct electrochemical sensing.

Sangeetha S. Patel, G. Krishnamurthy and Sabine Foro [52, 53] reported synthesis, crystal structure and electrochemical energy storage for some chelated Zn–metal–organic frameworks. They synthesized the chelated Zn-EDTA metal–organic framework (Zn–MOF) by an eco-friendly hydrothermal route at 160 °C and this product was confirmed by ATRIR, SEM, SXRD, TGA, and BET techniques. They investigated stability, homogeneous topology, significant surface area and electrochemical redox behaviour of the prepared Zn–MOF electrode in 0.005 M $K_4Fe(CN)_6$ solution by cyclic voltammetry. They observed that CV nature of Zn–MOF electrode showed the typical battery act from the surface redox reaction. They were also work on the charge–discharge study of chelated Zn–MOF electrode to find out the specific capacity of the Zn–MOF electrode in KOH solution at different temperatures and also in mixed electrolyte separately. In this work they found higher specific capacity of 243.2 mA hg^{-1} for the Zn–MOF electrode at room temperature in 0.1 M KOH at 1 Ag^{-1} and excellent capacity of about 589.28 mA hg^{-1} was found in mixed electrolytes. They concluded on these facts that the prepared Zn–MOF can be employed for energy (gas) storage application.

Arti Chouhan Ashutosh Pandey, Sadhana Singh and Subia Ambreen [54], reported a 4-pyridyltetrazole-based zinc metal-organic framework for photocatalytic degradation of methylene blue. They synthesized and characterized a metal–organic framework [mono(5-(4- pyridyl)tetrazolato) hydroxylzinc(II)] monoaqua (1) and observed an average particle size of the product was to be 43 nm by X-ray diffraction. They were also investigated efficacy of the synthesized MOF as a photocatalyst by taking a common wastewater dye methylene blue (MB) and observed that the photocatalytic activity MOF (1) has been found to be 86 % within one hour for 16 ppm of methylene blue (MB) dye using 0.8 g/L of catalyst. On the basis of these results, they concluded that the 4-pyridyltetrazole-based zinc metal-organic framework can be used for photocatalytic degradation of methylene blue.

Tia K. Tajnšek Erik, Svensson Grape and coworkers [55], reported an article related to design and degradation of permanently porous vitamin C and zinc-based metal-organic framework. In which they presented a Zn (II) bioMOF based on vitamin C as an independent ligand (bioNICS-1), that formed a three-dimensional chiral framework with permanent microporosity. They observed on the basis of comprehensive study of structure stability in bio relevant media in static and dynamic conditions, which demonstrate relatively high structure resistivity by retaining a high degree of its parent specific surface area. They also revealed that robustness of the 3D framework enables a slow degradation process, resulting in controllable release of bioactive components, which was confirmed by kinetic studies. Thus, on the basis of these facts, they concluded that BioNICS-1 can used for the designing of a small drug molecule delivery system

Enoch K Adotey et al [56], also published a research paper on zinc metal–organic framework with 3-pyridinecarboxaldehyde and trimesic acid as co-ligands for selective detection of Cr(VI) ions in aqueous solution. They suggested the use of simple organic ligands such as 3-pyridinecarboxaldehyde and trimesic acid with Zn(II) ion to fabricate a new MOF, that exhibited sensitive and selective luminescence quenching response towards CrO_4^{2-} and $Cr_2O_7^{2-}$ species in aqueous solution. They concluded on the basis of obtained results that the synthesized MOF could serve as a good luminescent sensor for CrO_4^{2-} and $Cr_2O_7^{2-}$ species in the contaminated aqueous phase.

The design of zinc metal organic frameworks for biomedical drug delivery were proposed by Bigness, Alec [57]. They prepared a vast library of zinc metal-organic frameworks (MOFs) and evaluated for their use in pharmaceutical drug delivery and modulated their properties and structures through at different reaction conditions like solvent, starting material ratios, and method of reaction. They also prepared a novel metal-organic framework, AB MOF1 and it was characterized by x-ray diffraction analysis. They evaluated that AB MOF1 was used for drug delivery in the model of pharmaceutical

drug ibuprofen for uptake studies. They were evaluated that AB MOF1's is stabile in common biological and medicinal solvents through Powder X-Ray Diffraction (PXRD). The Thermal Gravimetric Analysis (TGA) of AB MOF1 described that an evaporation of ibuprofen occurs at 157^{o}C during impregnated with ibuprofen and the change in morphology of AB MOF1 using PXRD give a similar indication that ibuprofen was absorbed by AB MOF1. In their article, computational DFT studies also revealed that the interaction between ibuprofen and AB MOF1 is favourable and the energy of interaction, which is defined as [(energy of AB MOF1 with ibuprofen) - (energy of ibuprofen alone + energy of AB MOF1 alone)], of the zinc paddlewheel motif and ibuprofen was found to be 1.030 kcal/mol. They concluded on the basis of these work that AB MOF1 can be used to uptake and release pharmaceutical drugs in a drug delivery vessel in biomedical applications.

Jisheng Xiao et al [58], reported some zinc-based metal–organic frameworks with tunable UV diffuse-reflectance as sunscreens. They have selected four types of zinc-based MOFs with various bandgap energies and investigated their optical behaviours along with their possibility as sunscreens. They found that zeolitic imidazolate framework-8 (ZIF-8) was possessed the highest and widest UV reflectance which protect against sunburn, DNA damage on mouse skin. They also achieved that this zeolitic imidazolate framework-8 (ZIF-8) has a comparable higher anti-UV efficacy relative to the commercially available UV filters, TiO_2 or ZnO, on pig skin. It was also observed by the authors that ZIF-8 exerted characteristics for topical skin use with low radical production, low skin penetration, low toxicity, high transparency, and high stability. On the basis of obtained results they concluded that ZIF-8 could potentially be a safe and effective sunscreen surrogate for human, and MOFs could be a novel source to develop more effective and safe UV filters

A team of Rosita Diana, Lucia Sessa, Simona Concilio, Stefano Piotto and Barbara Panunzi [59], were also reported luminescent Zn (II)-based nanoprobe, which is a highly symmetric supramolecular platform for sensing of biological targets and living cell imaging.

Cheng, Jiapeng et al [60], reported the synthesis of stable zinc-MOF materials by using fluorenone carboxylate ligand and expressed multifunctional detection and photocatalysis degradation property. They observed that this Zn-MOF is a fluorescent probe that can quickly recognize organic solvent nitrobenzene (NB) from other solvents under the detection limit of 2.9 μM, and Ksv (quenching efficiency) of 3.547×10^3 M^{-1} and it can also identify nitrobenzene derivatives, such as nitrophenol and nitrotoluene, with quenching efficiency of 16.54% and 92.64%, respectively and also Zn-MOF can be used to detect metal ions and has high selectivity for Al^{3+} and Fe^{3+} ions. They concluded on the basis of a series of experiments that other metal ions will not interfere with this detection and Zn-MOF can also be used as photocatalytic degradation of Rhodamine B (RhB), and in this case the photodegradation efficiency of RhB can reach 85% within 3 hours.

Mouhammad Abu Rasheed, Ahmad Alshaghel and Amir Alhaj Sakur [61], also reported a new type of zinc-based metal organic framework which worked as a stationary phase for thin layer chromatography. They synthesized a new type of zinc MOFs structure $Zn(BMAB).DMF]_n$ by using ultra sound assisted reaction process and described its utilization as a stationary phase for thin layer chromatography (TLC) which consists of chemically distinct binding groups 4-{[(1h-1,2,3-benzotriazol-1-yl)methyl]amino}benzoic acid (BMAB), and after using it can be activated via solvent exchange protocol to preserve its porous structure. They also characterized this MOF by using FT-IR, UV-diffuse reflection spectroscopy (UV-DRS) and differential scanning calorimetry (DSC). They also prepared TLC plates from the activated form of the structure to investigate its chromatographic characteristics by utilizing it to separate a model mixture of benzidine and o-tolidine using n-propanol: Chloroform: Acetonitrile (50:30:20, v/v/v) as a mobile phase. They observed the retardation factors (R_f), separation factor, and resolution (R_s) by densitometric method at 310 nm to be 0.45 and 0.63 (α=2.08, R_s=1.61) for o-tolidine and benzidine; respectively and concluded that the plate was then visualized using iodine chamber method to confirm a successful separation.

Wei-Ping Wu et al [62], reported the synthesis and application of a water stable zinc(II) glutamate metal organic framework for photocatalytic degradation of organic dyes. They synthesized a water stable metal-organic framework (MOF) with structural formula {[Zn(H2O)(L)]· xsolvent}n (L = glutamate) (1), in aqueous medium by simple mixing the Zn(II) salt and glutamate ligand at room temperature. They observed with the help of single crystal X-ray diffraction study that 1 crystallizes in an orthorhombic system with a space group of P212121 in which the Zn(II) centre adopts pseudo-octahedral geometry and bridging interactions through carboxylate groups in 1 and generates a 2D structure in 1 comprising of the microporous channels. They also performed UV/Vis diffuse-reflection spectroscopy for 1 which indicated that MOF possess semiconducting nature with a band gap of 3.23 eV. On the basis of these studies they revealed that it may be a used as photocatalyst.

Witri Wahyu Lestari [63-67], reported the synthesis of some new types of metal-organic frameworks based on zinc(II) and benzene-1,3,5-tricarboxylate modified graphite, fabrication and its application as an anode material in lithium-ion batteries. They were prepared these Zn-MOFs $[Zn_3(BTC)_2 12H_2O]$ (MOF 1) and $[Zn(BTC)H_2O3DMF]$ (MOF 2) using sonochemical and solvothermal methods. They were characterized the prepared materials by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric/differential thermal analysis (TG/DTA), and a battery analyzer. They used Rietica and Le Bail method to refine XRD data and observed that the sharp and intense

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peaks which indicated that the materials had a high degree of crystallinity. The morphology of the materials was found to be cubic as analysed by SEM, with an average crystal size of 8.377 4.276 m for MOF 1 and a larger size of 16.351 3.683 m for MOF 2. With the help of TGA they also found that MOF 1 was thermally stable up to 378.7 ^{O}C while MOF 2 remained stable up to 341.8 ^{O}C. They also observed that in a lithium ion battery, the synthesized materials as anode yield higher specific capacity and cycle stability compared to those using a graphite anode.

Ken Aldren S Usman et al [68-79], reported synthesis and characterization of zinc adeninate metal organic frameworks (biomof1) as potential anti-inflammatory. They were synthesized Zn8(ad)4(BPDC)6O•2Me2NH2 (bioMOF1) solvothermally at 130oC which is a porous metal–organic framework with zinc-adeninate secondary building units (SBUs), interconnected via biphenyldicarboxylate linkers and due to its non-toxic and biocompatible components (zinc and adenine) it can be used for drug delivery applications. They observed that bioMOF1 has a crystalline nature which was confirmed by using powder x-ray diffraction crystallography (PXRD) along with morphology assessment using focused-ion beam/field emission scanning electron microscopy (FIB/FESEM). They also introduced antiinflammatory drug, nimesulide (NIM) to the crystals via solvent exchange accompanied with vigorous stirring and quantified using thermogravimetric analysis (TGA) with loading saturation of ~30% attained during the 2nd to 3rd day of drug immersion. The kinetics of drug release in vitro was also done in phosphate buffer saline and in deionized water. They observed that the drug release showed a controlled discharge profile that reduced at one and two dayss of release. They detected that drug release in buffer showed a faster release of drug from the material. Slow drug release was observed for all of the set-ups with maximum % drug release of 24.47%, and 16.14% for the bioMOF1 in buffer and bioMOF1 in water respectively for the span of 48 hours.

Ying Jie Zhang, Lixian Sun and Fen Xu [80] reported synthesis, crystal structure and luminescence property on cabazoly-based zinc metal organic frameworks. They synthesized a novel zinc metal organic frameworks, ZnL(2,2′-bpy) with 3,6-dicarboxylic-9-ethylcarbazole acid (H_2L) as ligand. They characterized this type of ZnMOFs by FI-IR, elemental analysis, SEM, powder X-ray diffraction and single crystal X-ray diffraction to examine the structures. They also applied TG analysis to investigate the thermostability of Zn-MOFs. They observed that ZnMOFs possess triclinic crystal structure with a 1D chain that has distorted-octahedral coordination geometry. They also examined luminescent performance of ZnMOFs and concluded on the basis of obtained results that ZnMOFs can emit blue luminescence originating, which is assigned to the ligand-to-metal charge transfer (LMCT).

Tadeja Birsa et al [81-91], synthesized and structurally characterized new crystalline porous zinc benzene-1,3,5-tricarboxylate (Zn-MOF). They prepared this material in water/ethanol solution at 448 K after 1 day and its structure was elucidated from synchrotron powder X-ray diffraction data (R3c, a=30.1003(3), c=6.9141(2) Å). They observed that the framework of the structure is built up from chains of ZnO4 and ZnO6 polyhedra which are further connected through the carboxylate anions into a 3-D porous structure and free water molecules are disordered in the pores. They also concluded with the help of thermal analyses of the material, made by TG and HT-XRD and hydrothermal tests in boiling water, that it has reversible water adsorption/desorption properties.

Nathalie Saffon-Merceron et al [92] reported an unusual 3d zinc-organic framework constructed from paddle-wheel based carboxylate sheets bridged by acetate ions. They synthesized a zinc-2,6-naphthalenedicarboxylate metal-organic framework, (H2NEt2)[Zn2(AcO)(NDC)2]·nDEF (1) (DEF = N,N-diethylformamide, AcO = acetate), solvothermally in the presence of small amounts of acetic acid and it was characterized by single crystal, powder X-ray diffraction and thermogravimetric analysis. They observed that the compound 1 is an anionic 3D paddle-wheel MOF, in which the zincnaphthalenedicarboxylate sheets are linked together by bridging a ate ions and it exhibits large square channels (1313 Å), which contain DEF molecules and alternatively, charge-balancing diethylammonium cations in situ generated by the hydrolysis of DEF under the solvothermal conditions used. They also found that anionic host framework of 1 is unstable upon removal of guest DEF molecules and concluded that host-guest hydrogen bond interactions are crucial for maintaining the structural integrity of this compound.

Rui Sun et al [93], also reported a binary zinc–cobalt metal–organic framework derived mesoporous $ZnCo_2O_4$@NC polyhedron as a high-performance lithium-ion battery anode. They prepared $ZnCo_2O_4$ nanoparticles encapsulated in nitrogen-doped carbon ($ZnCo_2O_4$@NC) polyhedrons through a facile two-step method. They found that this prepared products had a uniform size and consisted mainly of interconnected $ZnCo_2O_4$ nanoparticles (NPs), which were uniformly distributed in the materials. As a result of which, the $ZnCo_2O_4$@NC polyhedrons of ZnCo-700 show a superb specific capacity of approximately 1601 mA h g^{-1} over 50 cycles at 0.1 A g^{-1}. They also observed that a reversible capacity of 1082 mA h g^{-1} was retained after 300 cycles at 1 A g^{-1}, and a superb reversible capacity of 775 mA h g^{-1} was attained even when the current density was increased to 5 A g^{-1}. They concluded that these distinguished electrochemical properties could be ascribed mainly to the uniquely advantageous structural and compositional features.

Elliot J. Carrington et al [94-102], reported a synthesis of a new porous and highly flexible metal-organic framework (MOF) from the flexible asymmetric linker N-(4-Carboxyphenyl) succinamate (CSA) and heptanuclear zinc oxo-clusters of formula [Zn7O2(Carboxylate)10DMF2] involving two coordinated terminal DMF ligands and its

anisotropic dynamic responses exhibited during the guest removal and single crystal coordinated solvent exchange. They observed that structural response of this MOF to the removal or exchange of its guest molecules has been explored to using a combination of experimental and computational approaches and the topology of the material, involving double linker connections in the a and b directions and single linker connections along the c axis, is shown to be key in the materials anisotropic response. They described that a and b directions remain locked during guest removal, while the c axis linker undergoes large changes significantly reducing the material's void space and the changes to the c axis linker involve a combination of a center motion on the linker's rigid side and conformational rearrangements on its flexible end. They concluded on the obtained facts that this was inactive during guest removal and the flexible ends of the a and b axis linkers are observed to play a prominent role during DMF to DMSO solvent exchange which facilitate the exchange reaction arising in the cluster.

Chouman, Ali Mouries et al [103]**,** reported a work related to superior removal of arsenic and lead from water using zinc-based metal organic framework ZN-MOF-74. They investigated the removal of As(V) and Pb(II) from aqueous media using the water-stable zinc-metal organic frameworks (Zn-MOF-74) prepared via room-temperature precipitation (RT-Zn-MOF-74) and solvothermal procedure (HT-Zn-MOF-74). They observed that the Zn-MOF-74 crystals possess an average particle size of 66 nm and 144 µm for RT-Zn-MOF-74 and HT-Zn-MOF-74, respectively. They also observed that nano-sized RT-Zn-MOF-74 exhibited superior performance to that of HT-Zn-MOF-74 but the BET surface area of the RT-Zn-MOF-74 was smaller than the HT-Zn-MOF-74. They revealed on the basis of adsorption isotherm studies that Langmuir isotherm was effective for the adsorption of As(V) onto RT-Zn-MOF-74 and HT-Zn-MOF-74 and Langmuir model was also describe the Pb(II) removal using both RT and HT Zn-MOF-74 with adsorption capacities capacity (qmax) value of 487 mg g-1 and 329.13 mg g-1 respectively. They concluded from the obtained results that it is the highest reported lead adsorption capacity in the literature and this study constitutes a direct evidence for the importance of tuning the size of MOF crystals to enhance.

Gee W J, Wells S A, Teat S J Raithby P R and Burrows A D [104] reported the synthesis of a new tripodal tricarboxylic acid ligand, 4,4′-(4′-(4′-carboxy-[1,1′-biphenyl]-4-yl)-[2,2′:6′,2″-terpyridine]-5,5″-diyl)-dibenzoic acid (H3cbt) and they obtained three types of metal-organic frameworks (MOFs) by subsequent reactions with zinc(ii) nitrate hexahydrate. They observed that these three MOFs, [Zn(Hcbt)]·4DMF (1), [Zn(Hcbt)]·4DMSO·1.5H2O·DMF (2) and [Zn(Hcbt)]·2DMF·3H2O (3), possessed flexible interdigitated 2D net topologies and they revealed that framework (1) has DMF-filled channels that retain porosity upon desolvation, with a measured BET surface area of 248 m2 g-1, framework (2) possesses larger DMSO-containing channels that collapse upon desolvation, resulting in near-equivalent porosity values to framework (1) and framework (3) contains a unique carboxylate binding mode which formed when wet solvents were used to synthesise (1) that precludes its subsequent adoption by either (1) or (2) upon their exposure to water. They concluded that these MOFs family with this type of structural considerations can be recommended for modelling using GASP.

Crawford, Scott E. et al [105], also reported a zinc-adeninate metal–organic framework which is a versatile photoluminescent sensor for rare earth elements in aqueous systems. As the rare earth elements (REEs) are critically important for national security and advanced technologies, they suggested a BioMOF-100 can be used as a fluorescent-based sensitizer for emissive REE ion detection in water, to increase the REE domestic production by different methods including the extraction of REEs from coal, coal combustion by-products and waste streams such as acid mine drainage, which provide rapid (<10 min) analysis times and sensitive detection (parts-per-billion detection limits) for terbium, dysprosium, samarium, europium, ytterbium, and neodymium, even in the presence of acids or secondary metals.

Abuzalat, Osama; Wong, Danny; Elsayed, Mohamed; Park, Simon; Kim, Seonghwan [106-111], reported sonochemical fabrication of Cu(II) and Zn(II) metal-organic framework films on metal substrates. In this article, they demonstrated a rapid and facile method for in-situ growth of metal-organic framework (MOF) films on Cu or Zn metal substrates by sonochemical techniques. In their work the substrates were first treated with a strong oxidizing agent to convert the metal to the corresponding metal hydroxide in the presence of ultrasonic irradiation which provide energy to drive the reaction between the metal ion sources and organic ligands. They observed that four MOF films (Cu-BTC, Cu-BDC, ZIF-8 and MOF-5) were successfully fabricated by this approach and these produced films were characterized by scanning electron microscopy and x-ray diffraction analysis. They concluded after investigating the effects of organic ligand concentration and ultrasonic irradiation time on MOF film synthesis that this rapid and facile fabrication method could serve a new route to grow MOF films on various gas sensor surfaces.

Motakef Kazemi N. and Hajiashrafi Sh [112], reported preparation and evaluation of zinc oxide nanoparticles by thermal degradation method. They were synthesized metal-organic frameworks based on zinc metal [Zn2(bdc)2(dabco)]n by solution (at room temperature) and solvothermal (at 90 ° C) after that they dissolved zinc oxide nanoparticles (ZnO) by thermal degradation. They were investigated these samples by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray diffusion spectroscopy (EDS) and Diffuse reflection spectroscopy (DRS). They also examine antibacterial activity of zinc oxide nanoparticles against Escherichia coli (E. coli). They concluded on the basis of the obtained results that thermal

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degradation of metal-organic frameworks based on zinc metal can be used successfully to preparation of zinc oxide nanoparticles and final nanoparticles have an appropriate antibacterial activity against E. coli and UV-blocking, can have a good potential for different applications.

Sharani Roy, Christopher B. George and Mark A. Ratner [113], reported a work related to catalysis by a zinc-porphyrin-based metal-organic framework from theory to computational design. They reported a detailed theoretical investigation of the framework-promoted reaction using the full atomic structure of the MOF and developed the three-step first-principles-based method for this purpose. They described on the basis of calculations that reactants bind to the closely packed porphyrin-Zn sites of ZnPO-MOF, resulting in a high local concentration of catalyst-bound reactant and they suggested a model predicting that reactant preconcentration in ZnPO-MOF can increase the initial rate of the acyl-transfer reaction by about 2 orders of magnitude relative to the uncatalyzed reaction.

LIU Zengxin, WANG Yijun, HAO Chunlian and LIU Xiuping [114] were also synthesized a MOF $\{[Zn_2(\mathbf{N})\cdot (DMF)_3\cdot (CH_3)_2NH_2]\cdot (DMF)_2\}_n$ (NEM-7-Zn) by nitrogen sites and —COO^- groups decorated ligand. They improve the stability by converting the metal center of NEM-7-Zn from Zn to Cu through metal ion exchange, which resulted in a stable skeleton (NEM-7-Cu). They were characterized this synthesized materials EA, PXRD, TGA and specific surface area analysis. They observed with the help of gas adsorption test results that NEM-7-Cu possesses high CO_2 uptake (74 $cm^3\cdot g^{-1}$) and selectivities for CO_2/CH_4 (11.5) and C_2H_2/CH_4 (7.1). They also revealed with the help of Grand canonical Monte Carlo (GCMC) simulations that the strong CO_2 adsorption sites exist near the Cu^{II} cluster sites, the uncoordinated —COO^- groups and the Lewis basic nitrogen sites.

Andrew D. Burrows, Laura C. Fisher, Timothy J. Mays, Sean P. Rigby, Sharon E. Ashbrook and Daniel M. Dawsond [115-129], reported a post-synthetic modification of zinc metal-organic frameworks through palladium catalysed carbon-carbon bond formation. They use post-synthetic Suzuki coupling reactions for the halide-functionalised metal-organic frameworks (MOFs) [Zn4O(bdc-Br)3] (bdc-Br = 2-bromo-1,4- benzenedicarboxylate, IRMOF-2) and [Zn4O(bdc-I)3] (bdc-I = 2-iodo-1,4- benzenedicarboxylate). They observed that the bulky catalyst employed leads to relatively low conversions and concluded that the reactions are not confined to the crystal surfaces after using the core-shell MOFs.

Javier Enríquez et al [130-135], reported controlled growth of the noncentrosymmetric Zn(3-ptz)2 and Zn(OH)(3-ptz) metal−organic frameworks. They proposed that noncentrosymmetric single-crystal metal−organic frameworks (MOFs) are suitable for phase matched nonlinear optical communication but in the case of typical hydrothermal synthesis conditions, there observed small crystals with relatively low transmittance and poor phase matching. In the search for optimal crystal morphology, they were study the effect of the metal-to-ligand molar ratio and reaction pH on the hydrothermal synthesis of the noncentrosymmetric Zn(3-ptz)2 and Zn(OH)(3-ptz) MOFs with in situ ligand formation. They found that in acidic environments, decrease in the amount of ligand below the stoichiometric molar ratio 1:2 also produces highly transparent single-crystal octahedrons of Zn(3-ptz)2 and in alkaline environments, they obtained long rodlike Zn(OH)(3-ptz) crystals whose length exceeds previous reports by up to 4 orders of magnitude. They characterized all reaction products by using powder X-ray diffraction, Fourier transform infrared spectroscopy, optical and scanning electron microscopy, and solid-state UV−visible spectroscopy. They concluded on the basis of the obtained results that the proposed synthesis could be an alternative synthesis route for the recently reported high-energy MOF Zn(3-ptz)N3 and this can be used to develop MOF-based nonlinear optical devices.

M. Zhao, J. Su, J. Zhang, J.-Y. Wu and Y.-P. Tian [136] reported a metal-organic framework with a novel topology, poly[sesqui(μ_2-4,4'-bipyridine)bis(dimethylformamide)bis(μ_4-4,4',4"-nitrilotribenzoato)trizinc(II)], $[Zn_3(C_{21}H_{12}NO_6)_2(C_{10}H_8N_2)_{1.5}(C_3H_7NO)_2]_n$, that was obtained by the solvothermal method using 4,4',4"-nitrilotribenzoic acid and 4,4'-bipyridine (bipy). They determined its structure byusing single-crystal X-ray diffraction analysis and found that this structure possesses three types of crystallographically independent Zn^{II} cations and binuclear $Zn_2(COO)_4(bipy)_2$ paddle-wheel clusters. They concluded that it 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.

Lysova, A., Samsonenko, D., Dybtsev, D., and Fedin, V [136], reported the synthesis and luminescence properties of new type of metal-organic frameworks based on zinc(II) ions and 2,5-thiophendicarboxylate ligands. They prepared six new types of metal-organic frameworks based on 2,5-thiophendicarboxylate (tdc^{2-}) and zinc(II) ions in different reaction conditions, and were determined their crystal structures by XRD analysis. They observed that the compound $[Zn(tdc)(dabco)(H_2O)]\cdot DMF$ (1) is based on mononuclear Zn(II) ions connected by tdc^{2-} and dabco linkers into square-grid layered nets, the compound $[Zn_3(tdc)_3(dabco)_2]$ (2) is a rare example of monocoordinated dabco ligands in the metal-organic framework chemistry in which its crystal structure contains trinuclear linear carboxylate building units, connected into a distorted primitive cubic net, $[Zn_5(tdc)_4(Htdc)_2(dabco)_2]\cdot 4DMF\cdot 14H_2O$ (3) has a same structure as (2) although as a part of more complicated pentanuclear motives, the compound $[Na_2Zn(tdc)_2(DMF)_2]$ (4), quantitatively isolated by the addition of NaOH to the mixture of $Zn(NO_3)_2$ and H_2tdc, is based on 1D chain motives, interconnected by tdc^{2-} linkers into a three-dimensional framework and the compounds $[Zn_3(tdc)_3(DMF)_2]\cdot 0.8DMF\cdot 1.1H_2O$ (5) and $[Zn_3(tdc)_3(DMF)_3]\cdot 0.8DMF\cdot 1.3H_2O$ (6) were prepared in very similar reaction conditions,

but with different times of heating, indirectly indicating higher thermodynamic stability of the three-dimensional metal-organic framework (6), compared to the two-dimensional metal-organic framework (5) and also the crystal structures of both (5) and (6) are based on the same trinuclear linear units as in (2). They also studied luminescence properties of the compounds (4), (5) and (6) were and compared with those for Na_2tdc salt and observed that the luminescence spectra of (4) practically coincide with those for the reference Na_2tdc, while (5) and (6) exhibit coherent shifts of peaks to higher energies. They concluded that such hypsochromic shifts are likely associated with a different effective charge on the tdc^{2-} anions in Na_2tdc and sodium-containing (4), compared to zinc-based (5) and (6).

III. CONCLUSION OF PROPOSED REVIEW AND FUTURE OUTLOOK

Zinc based metal-organic frameworks synthesis and their applications such as, their utility for removal and detection of antibiotics in water, for detection and differentiation of Fe(III) and Cr(VI) ions in aqueous solution, as an efficient catalyst, as photocatalyst, removal of emerging drug contaminant (amodiaquine) from aqueous solution, in drug delivery, cell imaging and sensing, as nontoxic and biodegradable platforms for biomedical applications, as an electrode material for hydrazine sensing. Zn-MOFs have attracted considerable attention in synthetic chemistry and medicinal chemistry as well as in material chemistry. This review highlighted research work of many researchers reported in literature for synthesis, properties and different application. From this review it may be concluded that the modification in Zn-MOFs displayed valuable physiochemical and pharmacological activities and these modifications can be utilized to develop potentially biologically active agents for future investigations. This review can be helpful to develop various new compounds possessing Zn-MOFs moiety that could be better in terms of efficiency and safe therapeutic agents of clinical importance.

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