

# **APPLICATION OF POROUS METAL ORGANIC FRAMEWORKS**

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**DEPARTMENT OF CHEMISTRY  
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# **Application of Porous Metal Organic Frameworks**

**by**

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**to the**



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## CERTIFICATE

This is to certify that the thesis entitled, “**Application of porous metal organic frameworks**” being submitted by **Ms. Manju Srivastava** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. **Ms. Manju Srivastava** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or full, to any other university or institute for award of any degree or diploma.

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## **Dedication**

*To my mentor, guide, and spiritual guru  
Most Revered Prof. Prem Saran Satsangi Sahab*

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## ABSTRACT

Metal organic frameworks (MOFs) belong to the emerging class of porous materials, which in view of their high surface areas, thermal stability and uniform pore size appear to be excellent candidates for various applications including gas storage, separation, sensing and catalysis. The availability of in-pore functionality and possibility of outer-surface modification in MOFs render these materials expedient over aluminosilicates such as zeolites for specific applications. Furthermore, it is possible to tune the pore size and geometry of MOFs, by judicious choice of metal ion and the organic linker units.

There is abundant empirical literature, where MOFs with tailorable uniform pore size have been prepared, which exhibit extremely high surface area, selective uptake of small molecules and optical or magnetic response upon inclusion of guest molecules. Transition metal ions with varying oxidation states and geometries have been used as inorganic constituent of MOFs. In general, rigid ligands are preferred as organic linkers for synthesizing MOFs, as the inherent rigidity of the resulting framework permits the sustenance of the open-pore structure after removal of the solvent, which remains entrapped during the reaction. The linkers can be electrically neutral, anionic or cationic. The purity requirement of reagents for preparation of MOFs is rather stringent, i.e. the ligand, metal ion and even the solvent need to be extremely pure to avoid competitive reactions. The presence of even small amounts of impurities e.g. water in DMF, has been reported to lead to the formation of competitive phases.

For the last two decades, the field of MOFs has seen rapid growth, primarily related to the design of new MOFs and exploring their potential for different applications. What renders MOF interesting is their hybrid nature, which results from the combination of both inorganic metal ions as well as the organic linker. However, their commercial application is still in the stage of infancy.

Chapter 1 provides a brief account of the literature survey performed on selected MOFs. The type of ligands and metal ions used for preparation of MOFs has been

discussed. The underlying motivation behind the present work has also been brought out in this chapter.

Chapter 2 discusses the results of our studies on the structural landscape of MOF 5, perhaps the most celebrated MOF prepared through the supramolecular assembly of zinc ions with benzene dicarboxylic acid. This chapter has been subdivided in two sections. Part A deals with the influence of water in DMF during the preparation of MOF 5. The hydrolytic decomposition of DMF under solvothermal conditions led to the formation of formate and dimethyl ammonium ions in the reaction medium, which altered the course of crystallization resulting in the formation of different competitive phases.

Chapter 3 discusses our attempts at deriving a high purity ligand (benzene dicarboxylic acid) from polyethylene terephthalate (PET) wastes. A microwave assisted alkalolytic procedure was explored for tertiary recycling of PET which led to the formation of high purity BDC. The same was subsequently used for the synthesis of two MOFs, namely copper benzene dicarboxylate Cu(BDC) and  $Zn_4O(BDC)_3$  [MOF 5].

In chapter 4, we have demonstrated the applicability of core-shell MOFs for use as a stationary phase towards aiding gas chromatographic separations. Techniques for large-scale preparation of MOFs at gram level generally rely on solvothermal methods, which lead to the formation of crystalline powder with particle size almost always lower than 0.5 microns, which result in huge pressure drop when filled in packed chromatographic columns. For using MOFs in GC packed columns, it is imperative to increase their particle size. In this context, we have prepared core-shell structures, where the shell region comprises of MOF 5 and ZIF 8, with the core (polydimethylsilicone) being a result of suspension polymerisation of the vinyl macromonomer. In the subsequent section we have discussed representative chromatographic separations obtained with MOF 5@PDMS and ZIF 8@PDMS. In view of the hydrolytic stability of ZIF-8, the same could be used for effecting separations of aqueous media, an application not accomplishable with water-sensitive MOF-5.

In Chapter 5, we have demonstrated the potential of MOFs in the context of epoxy toughening, by preparing epoxy-MOF 5 composites and systematically studying the mechanical properties of the resulting composites.

Chapter 6 presents our results on the adsorption of toluene on MOF 5, HKUST 1 and ZIF 8, a common pollutant in air.

The summary and conclusions drawn from the studies performed during this research work are discussed in Chapter 7. In addition, key areas, where future work needs to be carried out are also highlighted.

## सार

धातु कार्बनिक फ्रेमवर्क (एमओएफ) झरझरा सामग्री के उभरते हुए वर्ग से संबंधित हैं, जो अपने उच्च सतह क्षेत्रों, थर्मल स्थिरता और वर्दी के आकार का आकार गैस भंडारण, जुदाई, संवेदन और उत्प्रेरक सहित विभिन्न अनुप्रयोगों के लिए उत्कृष्ट उम्मीदवार मानते हैं। एमओएफ में बाहरी सतह की संशोधितता की उपलब्धता और इसकी उपलब्धता की उपलब्धता, इन विशेषताओं के लिए जिओलिटियों जैसे एल्यूमीनोसिलिसेट्स के अनुकूल है। इसके अलावा, धातु आयन और कार्बनिक लिंकर इकाइयों की समझदारी से, एमओएफ के ताकना आकार और ज्यामिति को ट्यून करना संभव है।

प्रचुर मात्रा में अनुभवजन्य साहित्य हैं, जहां टेलरमर वर्दी की ताकना आकार के साथ एमओएफ तैयार किया गया है, जो अति उच्च सतह क्षेत्र, छोटे अणुओं की चयनात्मक तेजता और अतिथि अणुओं को शामिल करने पर ऑप्टिकल या चुंबकीय प्रतिक्रिया का प्रदर्शन करते हैं। ऑक्सीकरण राज्यों और ज्यामितिओं के साथ संक्रमण धातु आयनों का उपयोग एमओएफ के अकार्बनिक घटक के रूप में किया गया है। सामान्य तौर पर, कठोर ligands को MOFs के संश्लेषण के लिए जैविक लिंकर के रूप में प्राथमिकता दी जाती है, क्योंकि परिणामी रूपरेखा की अंतर्निहित कठोरता विलायक को हटाने के बाद खुले-ताकना ढांचे के संरक्षण की अनुमति देती है, जो प्रतिक्रिया के दौरान फंसे रहती है। लिंकर विद्युत रूप से तटस्थ, एनोनिक या cationic हो सकते हैं। एमओएफ तैयार करने के लिए अभिकर्मकों की शुद्धता की आवश्यकता सख्त होती है, अर्थात् लिगेंड, धातु आयन और यहां तक कि विलायक को प्रतिस्पर्धी प्रतिक्रियाओं से बचने के लिए बेहद शुद्ध होना चाहिए। अशुद्धियों की थोड़ी मात्रा की उपस्थिति उदा। डीएमएफ में पानी, प्रतिस्पर्धी चरणों के गठन के लिए नेतृत्व करने के लिए रिपोर्ट किया गया है

पिछले दो दशकों से, एमओएफ के क्षेत्र में तेजी से वृद्धि हुई है, मुख्य रूप से नए एमओएफ के डिजाइन से संबंधित है और विभिन्न अनुप्रयोगों के लिए उनकी क्षमता की खोज की जा रही है। क्या एमओएफ दिलचस्प बनाता है उनकी हाइब्रिड प्रकृति है, जो अकार्बनिक धातु आयनों के साथ-साथ कार्बनिक लिंकर दोनों के संयोजन से होती है। हालांकि, उनका वाणिज्यिक आवेदन अभी भी प्रारंभिक अवस्था में है।

अध्याय 1 चयनित एमओएफ पर किए गए साहित्य सर्वेक्षण का संक्षिप्त विवरण प्रदान करता है। एमओएफ की तैयारी के लिए इस्तेमाल किए जाने वाले लिगंड्स और धातु आयनों के प्रकार पर चर्चा की गई है। वर्तमान कार्य के पीछे मूल प्रेरणा भी इस अध्याय में लाई गई है।

अध्याय 2, एमओएफ 5 के संरचनात्मक परिदृश्य पर हमारे अध्ययन के परिणामों पर चर्चा करता है, शायद बेज़िन डिकारबैक्जिलिक एसिड के साथ जस्ता आयनों के सुप्रामोलेकुलर असेंबली के माध्यम से तैयार सबसे मशहूर एमओएफ। इस अध्याय को दो खंडों में विभाजित किया गया है। एमओएफ 5 की तैयारी के दौरान डीएमएफ में पानी के प्रभाव के साथ भाग ए सौदों की वजह से डीएलएफ के हाइड्रोलाइटिक अपघटन के कारण प्रतिक्रिया माध्यम में फार्मेट और डाइमिथाइल अमोनियम आयनों का गठन हुआ, जिसके परिणामस्वरूप क्रिस्टलीकरण के निर्माण में परिवर्तन हुआ। विभिन्न प्रतिस्पर्धी चरणों का

अध्याय 3 पॉलीथीन टेरैफेथलेट (पीईटी) कचरे से उच्च शुद्धता लिगेंड (बेज़ीन डायआर्बैक्जिलिक एसिड) लाने पर हमारे प्रयासों की चर्चा करता है। पीईटी की तृतीयक रीसाइक्लिंग के लिए एक माइक्रोवेव की सहायता की एल्कोलोलिटिक प्रक्रिया का पता लगाया गया जिससे उच्च शुद्धता बीडीसी के गठन का कारण आ गया। बाद में इसका इस्तेमाल दो एमओएफ के संश्लेषण के लिए किया गया, अर्थात् तांबा बेज़ीन डायआर्कबॉक्सलाइट क्यू (बीडीसी) और जेडएन 4 ओ (बीडीसी) 3 [एमओएफ 5]।

अध्याय 4 में, हमने गैस-क्रोमेटोग्राफिक अलग-अलग सहायता के लिए एक स्थिर चरण के रूप में उपयोग के लिए कोर-शेल एमओएफएस के प्रयोज्यता का प्रदर्शन किया है। ग्राम स्तर पर एमओएफ की बड़े पैमाने पर तैयारी के लिए तकनीक आम तौर पर सॉलवोथर्मल तरीकों पर भरोसा करती है, जो कण आकार के साथ क्रिस्टलीय पाउडर के गठन से लगभग हमेशा 0.5 माइक्रोन से कम होती है, जिसके परिणामस्वरूप पैक क्रोमेटोग्राफिक स्तंभों में भरा हुआ भारी दबाव ड्रॉप होता है। जीसी पैक किए गए कॉलम में एमओएफ का उपयोग करने के लिए, उनके कण आकार को बढ़ाने के लिए आवश्यक है इस संदर्भ में, हमने कोर-शेल संरचनाओं को तैयार किया है, जहां शेल क्षेत्र में एमओएफ 5 और जेआईएफ 8 शामिल हैं, जिसमें कोर (पॉलिडीमेथाइलसिइलकोन) विन्नील मैक्रोमोनेमोर के निलंबन पॉलिमरीकरण का परिणाम है। बाद के खंड में हमने एमओएफ 5 @ पीडीएमएस और जीआईएफ 8 पीडीएमएस के साथ प्राप्त प्रतिनिधि क्रोमेटोग्राफिक अलग-अलग चर्चा की है। जेआईएफ -8 की हाइड्रोलाइटिक स्थिरता को देखते हुए, जलीय मीडिया के पृथक्करण को प्रभावित करने के लिए इसका इस्तेमाल किया जा सकता है, जो पानी के प्रति संवेदनशील एमओएफ -5 के साथ लागू नहीं है।

अध्याय 5 में, हमने ईपीओसी-एमओएफ 5 कंपोजिट तैयार करके और परिणामी कंपोजिट के यांत्रिक गुणों का अध्ययन करते हुए, एपोक्नी टौफेनिंग के संदर्भ में एमओएफ की क्षमता का प्रदर्शन किया है।

अध्याय 6 हमारे परिणामों को एमओएफ 5, HKUST 1 और ZIF 8, हवा में आम प्रदूषक पर टोल्यूनि के सोखना पर प्रस्तुत करता है।

इस शोध कार्य के दौरान किए गए अध्ययनों से तैयार सारांश और निष्कर्षों को अध्याय 7 में चर्चा की गई है। इसके अलावा, मुख्य क्षेत्रों, जहां भविष्य के कामों को पूरा करने की जरूरत है, को भी प्रकाश डाला गया है।

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## Abbreviations

- 1) BDC = Benzene dicarboxylic acid
- 2) MeIm = Methyl imidazole
- 3) PhIm = Phenyl imidazole
- 4) Im = Imidazole
- 5) BTC = Benzene tricarboxylic acid
- 6) DABCO = 1,4-Diazabicyclo[2.2.2]octane
- 7) DMF = Dimethyl formamide
- 8) H2hfipbb = 4,4'-(hexafluoroisopropylidene) bis(benzoic acid)
- 9) 4,4'-bipy = 4,4'-Bipyridine
- 10) IRMOF = Isoreticular Metal organic framework
- 11) MIL = Material Institute Lavoisier
- 12) ZIF = Zeolitic imidazolate framework
- 13) UIO= University of Oslo
- 14) HKUST = Honk Kong University of Science and Technology
- 15) TETA= Triethyl tetra amine
- 16) SHPB = Split Hopkinson Pressure Bar
- 17) ASTM = American Society for Testing and Materials
- 18) CP = Coordination polymers
- 19) MOF = Metal organic framework
- 20) PCP = Porous coordination polymers
- 21) SBU = Secondary building unit

- 22) TLC = Thin layer chromatography
- 23) VOC = Volatile Organic Compound
- 24) PXRD = Powder X-ray diffraction
- 25) HPLC = High performance liquid chromatography
- 26) FTIR = Fourier transform infrared
- 27) ATR = Attenuated total reflectance
- 28) EG = Ethylene glycol
- 29) PET = Poly(ethylene terephthalate)
- 30) SEM = Scanning electron microscopy
- 31) PDMS = Poly(dimethylsiloxane)
- 32) FID = Flame ionization detector
- 33) CNT = Carbon nanotubes
- 34) SBA = Santa Barbara Amorphous