Metal Organic Materials (MOMs) for Environmental, Biological and Catalytic Applications

A Thesis
submitted
by

Darsi Rambabu

(Roll No: D12055)

for the award of the degree of

Doctor of Philosophy

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Affectionately

Dedicated

To

My

Almighty God

(Śrī Rāma)

"An equation for me has no meaning unless it represents a thought of God"

– Srinivasa Ramanujan

Declaration by the Research Scholar

This is to certify that the thesis entitled **"Metal Organic Materials (MOMs) for Environmental, Biological and Catalytic Applications"**, submitted by me to the Indian Institute of Technology, Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Abhimanew Dhir and Dr. Pradeep C. Parameswaran. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

I.I.T. Mandi (H.P.)

Date:

Signature of Research Scholar

Darsi Rambabu

Thesis Certificate

This is to certify that the thesis entitled "**Metal Organic Materials (MOMs) for Environmental, Biological and Catalytic Applications"**, submitted by Mr. Darsi Rambabu to the Indian Institute of Technology, Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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I.I.T. Mandi (H.P.)

Date:

Research Guide

Dr. Abhimanew Dhir

Dr. Pradeep C. Parameswaran (*co-guide*)

Indian Institute of Technology Mandi, V.P.O. Kamand, Tehsil Sadar, Near Kataula, Parashar Road, Mandi, Himachal Pradesh 175005. Telephone No.01905-237143, 01905-267045,
Email: abhimanew@iitmandi.ac.in, pradeep@iitmandi.ac.in

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Abbreviations

1D	1-dimensional
2D	2-dimensional
3D	3-dimensional
˚ C	degrees centigrade
4-AP	4-aminophenol
2,6-ndc	2,6-naphthalenedicarboxylate
4-NP	4-nitrophenol
AB	Azobenzene
Al	Aluminium
Ag	Silver
Au	Gold
AYGG	Alizarin yellow GG
Ba	Barium
BDC	benzenedicarboxylic acid
BDTriP	5,5′-(5-(1H-pyrazol-4-yl)-1,3-phenylene)bis(1H-1,2,3-triazole)
BPDC	biphenyl-4,4′-dicarboxylate
BTAC	benzene-1,3,5-tri-β-acrylate
BTC	1,3,5-benzenetricarboxylic acid
BTB	1,3,5-benzenetribenzoate
BTE	4,4',4"-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzoic acid
BTT	1,3,5-benzenetristetrazolate
BTEC	1,2,4,5-benzenetetracarboxylate

bipy	4,4’ –bipydine
BY	Brilliant yellow
CCD	charge coupled device
CCDC	Cambridge Crystallographic Data Centre
Cd	Cadmium
CPs	coordination polymers
Cr	Chromium
Cu	Copper
CH_4	Methane
CHEF	chelation enhanced fluorescence
Cl	Chorine
Co	Cobalt
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
cm	centimeter
cyt c	Cytochrome c
dabco	1,4-diazabicyclo[2.2.2]octane)
DASS-Na	4,4’-diaminotrans-stilbene-2,2’-disulfonate disodium hydrate
DCM	Dichloromethane
d/nm	Diameter in nanometer
DLS	Dynamic light scattering
DMF	N,N-dimethylformamide
def	N,N-diethylformamide

DMSO	Dimethyl sulfoxide
DOE	Department of Energy
DW	Distilled Water
Dy	Dysprosium
EDX	Energy Dispersive Analysis of X-rays
Eu	Europium
Fe	Iron
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
$g\ L^{-1}$	gram per liter
Gd	Gadolinium
K	kelvin
HRTEM	High resolution transmission electron microscopy
H_2	Hydrogen
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
IC_{50}	half maximal inhibitory concentration
IR	Infrared
LED	light emitting diode
LAG	liquid-assisted grinding (LAG)
LOD	Limit of detection
mg	Milligram
$mg\ g^{-1}$	Milligram per gram
mdip	5,5’-methylene diisophthalate

min	minute
ml	Milliliter
mM	Millimolar
Mo	Molybdenum
MO	Methyl orange
MO1	Mordant orange 1
MOF	Metal organic framework
MOG	Metal organic gel
mol kg^{-1}	mole per kilogram
MOM	Metal organic material
MOXG	Metal organic xerogel
Mn	Manganese
MPa	mega pascals
MTB	methanetetrabenzoic acid
MW	Molecular weight
Na	Sodium
Ni	Nickel
nm	Nanometer
NMR	Nuclear magnetic resonance
NPs	Nanoparticles
ns	nano seconds
N_2	Nitrogen
NTB	4,4',4"-nitrilotrisbenzoic acid

O_2	Oxygen
OG	Orange G
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Θ	Theta
PAP	4-Phenylazophenol
Pd	Palladium
PDI	Polydispersity index
Pt	Platinum
PTS	1,3,6,8–pyrenetetrasulfonic acid tetra sodium salt
PXRD	Powder x-ray diffraction
QN	quinoline
Rh	Rhodium
RPM	Revolutions per minute
Ru	Ruthinium
RT	Room temperature
RW	River water
SII	Sudan II
STP	standard temperatures and pressures
SC	4-sulfocalix[4]arene
SV	Stern–Volmer
SXRD	Single crystal x-ray diffraction
T	Temperature
Tb	Terbium

TDPAT	2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine
TFPI	Tissue Factor Pathway Inhibitor
THF	Tetrahydrofuran
TCA	thiacalix[4]arene
TEM	Transmission electron microscopy
TGA-DSC	Thermal gravimetric analysis coupled with differential scanning calorimetry
$tatb^{3-}$	4,4',4''-s-triazine-2,4,6-triyltribenzoate
Ti	Titanium
TONa	Tropaeolin O sodium salt
TP	thromboplastin
UV	Ultraviolet
v	volume
V	Vanadium
Vis	Visible
wt%	Weight percentage
w/w	Weight to weight ratio
XRD	X-ray diffraction
Z-Average	Average of particles size
Zn	Zinc
Zr	Zirconium
α	Alpha
β	Beta
γ	Gaama

δ	Delta
λ	Wavelength
τ	Tau
μ	Micro
μg	Microgram
μL	Microliter
μm	Micrometer
μM	micro molar
χ	Khi

Materials and instrumentation used

Bovine heart Cytochrome c (Cyt c), 2, 6-napthlene dicarboxylic acid (H_2NDC), $Mn(NO_3)_2$ $4H_2O$, DMF, Na_2CO_3 (CO_3^{2-}), $NaClO_4$ (ClO_4^-), Na_2HPO_4 (HPO_4^{2-}) and tetrabutyl ammonium salts were purchased from Sigma Aldrich. HEPES purchased from Alfa Aesar. 1,3,6,8–pyrenetetrasulfonic acid tetra sodium salt was purchased from Sigma Aldrich. 4-sulfocalix[4]arene was purchased from Sigma Aldrich. All other chemicals and reagents were purchased from Sigma Aldrich.

The FTIR spectral studies were performed on Perkin Elmer FT-IR spectrometer using KBr pellets. Fluorescence studies were carried on Agilent Technologies cary eclipse fluorescence spectrophotometer. U.V studies were carried on SHIMADZU UV-2450 spectrophotometer using quartz cuvettes. The fluorescence life time was measured time correlated single photon counting (TCSPC) setup using LASER diode (405 nm) from ISS, USA (ehrones BH fluorescence life time spectrometer). The fluorescence life time was measured by time correlated single photon counting (TCSPC)-HORIBA scientific (Delta Flex system) setup using 390 nm Nano LED. Single crystal X-ray details along with CCDC numbers are given in respective chapters. Powder X-ray diffraction (PXRD) data was collected on Rigaku SmartLab 9 KW rotating anode Powder X-ray diffractometer at room temperature. TEM images collected on SEI TECNAI F20 HRTEM (high resolution transmission electron microscope). The thermogravimetric analysis was carried out using Mettler Toledo thermal analyzer on N_2 atmosphere and heating speed 10 °K/ min. FESEM data was collected on Nova Nano SEM-450 JFEI modal of USA (S.E.A) PTE LTD. NMR data was collected on JNM ECX-500 modal of Joel India instrument. Stereo microscope images were collected on Magnuspro, modal x86 3.7.5501 of Magnus analytics.

Abstract

Metal organic materials (MOMs) are promising materials incredibly having wide range of utility in various fields such as magnetism, nonlinear optics, displays, gas purification, gas storage, biomedical applications and electroluminescent devices. MOMs are synthesized by connecting the organic moieties to inorganic species *via* covalent or non covalent interactions. Numerous MOMs have been reported till date including wide range of metals/metal nanoparticles with various organic linkers/macrocycles for diverse applications. However, still there is large scope of design and synthesis of new MOMs for their applications in the fields of environmental and biological science and catalysis.

In the present thesis, we have designed and synthesized different types of MOMs including metal organic frameworks (MOFs) and their hybrids, coordination polymers and self-assembled materials of metal nanoparticles and macrocycles particularly calix[4]arenes and thiacalix[4]arenes for diverse applications. The work is distributed in six different chapters from chapter 2 to chapter 7 excluding chapter 1 and chapter 8 which includes introduction and conclusions respectively.

One of the new significant areas related to porous MOFs being investigated is immobilization of bio-molecules in its pores. In this context, we have designed and synthesized an ensemble of cytochrome c with Mn(II) and 2,6-naphthalene dicarboxylate based MOF. The bio-material selectively senses sulfate ions in 100% aqueous solution and in solid phase with real world application. Further, to explore the utilization of MOMs for recognition of environmentally hazardous molecules, we synthesized a coordination polymer and metal organic xerogel based on pyrene tetrasulfonate and phenanthroline dicarboxylic acid respectively. These two MOMs are utilized as templates for recognition

of industrially relevant azo dyes. The real world application of these MOMs as azo dye sensor has been shown by detecting 'brilliant yellow' azo dye on fabric and in common food stuffs where azo dyes are used as adulterants. Xerogel is also evaluated for its catalytic activity in Knoevenagel condensation reaction. We further aimed for the biological applications of MOMs. Thus, we designed and synthesized 2,6 naphthalene dicarboxylate (NDC) and quinoline (QN) based Cd(II) coordination polymer $\{[Cd(NDC)(QN)]\}_n$. The synthesized coordination polymer behaves as synthetic blood anticoagulant. A group of pharmaceuticals called anticoagulants which prevent blood coagulation are developed as medication for disorders like thrombosis, pulmonary embolism, myocardial infarction and strokes. In next and final part of thesis, we have reported new self-assembled materials based on Pd and Ru nanoparticles using thiacalix[4]arenes and calix[4]arenes as templates for catalytic reduction of two environmental pollutants '4-nitrophenol' and 'brilliant yellow' azo dye respectively.