DECLARATION

I hereby declare that the thesis entitled "**Self-Assembly of Structurally Diverse Phosphomolybdates: Synthesis, Structure and Properties**", submitted to the University of Calicut in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry is a bonafide research work done by me under the supervision and guidance of Dr. Jency Thomas, Assistant Professor, Research & PG Department of Chemistry, St. Thomas College (Autonomous), Thrissur, Kerala.

I further declare that this thesis has not previously formed the basis of any degree, diploma or any other similar title.

Jisha Joseph

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"There's nothing more calming in difficult moments that knowing there's someone fighting with you"
- Mother Teresa

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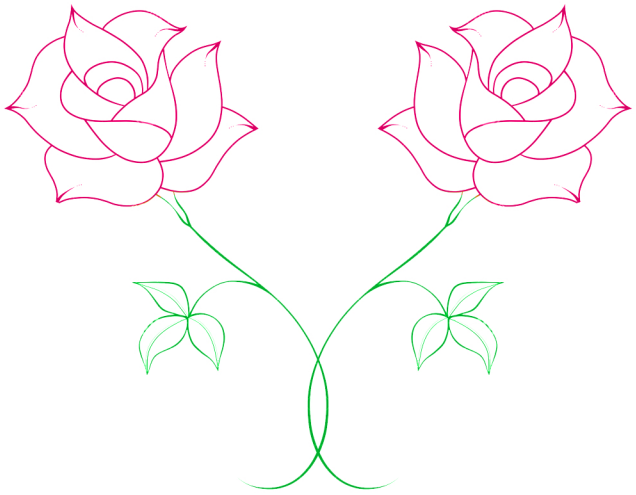
Jisha Joseph

Dedicated to,

Sacred Heart CMC Province
Mananthavady



As we express our gratitude,
we must never forget that
the highest appreciation is not
words, but to live by them.

John F Kennedy

PREFACE

Phosphomolybdate (PMO) is an important sub-class of Polyoxometalates (POMs). This phosphorous and molybdenum containing heteropolyanions comprise of a distinguished family with versatile structural features and promising applications. The counter cations of these anionic clusters can be metal ions, metal complexes or protonated organic moieties. The Phosphomolybdates are widely classified into various types. Among these, Strandberg-type $\{P_2Mo_5O_{23}\}^{6-}$, Keggin-type $\{PMo_{12}O_{40}\}^{3-}$, Wells Dawson-type $\{P_2Mo_{18}O_{62}\}^{6-}$ and as fully reduced cluster $\{P_4Mo_6O_{31}\}^{12-}$ are the predominant types. Since they are supramolecular materials they can self-assemble into tuneable size and shape with varying dimensionality. In this thesis, seven novel Strandberg-type PMOs and one copper based Keggin-type solid have been reported along with their characterization and related physico-chemical properties. Ammonium Phosphomolybdate (APM) which is a Keggin-type PMO was synthesized along with its two composites with polyaniline and poly (N-methylaniline), namely APM/PAni and APM/PNMAni respectively. APM was found to be a good ion-exchanger to remove cationic dye-stuffs from its aqueous solution with high efficiency and appreciable reusability. The Cr(VI) removal efficiency of APM and its composites have been investigated and APM/PNMAni was observed as a good candidate for the same.

Two synthetic methods have been used in the thesis namely, solvent evaporation technique and hydrothermal technique. In the first method, P and Mo precursors along with organic moiety and metal chlorides were taken in the form of clear aqueous solution and kept undisturbed for the self-assembly process. The slow evaporation of the solution at room temperature resulted in crystallization of PMO based solids. In the second method, a hydrothermal bomb was used; which is a sealed Teflon container. The reaction

was carried out under autogenous pressure and the precursors were added along with water. A temperature range from 100-180^{o}C was selected for a time span of 3 days. The slow cooling of the apparatus was allowed for the crystallization of solids.

The thesis is divided into seven chapters. Chapter I comprises of a brief introduction to the work, giving emphasis to the synthetic routes, different classes of PMOs based on their structural features and properties along with their important applications. A literature survey on the research carried out in this area for the past decade was carried out and systematically tabulated.

In chapter II, two new Strandberg cluster (referred to as $\{P_2Mo_5\}$) based PMOs namely, $\{H\text{-}2a3mp\}_5[\{PO_3(OH)\}\{PO_4\}Mo_5O_{15}]$, and $\{H\text{-}2a4mp\}_5[\{PO_3(OH)\}\ \{PO_4\}Mo_5O_{15}]$. $6H_2O$ were synthesized *via* solvent evaporation technique using 2-amino-3-methylpyridine (2*a*3*mp*) and 2-amino-4-methylpyridine (2*a*4*mp*) respectively. These solids formed a supramolecular framework stabilized by hydrogen bonding interaction between cluster anions and organic moieties. CH…π interactions between the organic moieties reinforced the crystal packing. The electrochemical behaviour of the synthesized solids was explored by means of three electrode system using 1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl as supporting electrolyte. In addition, the optical band gaps of the solids were also calculated using ultraviolet-diffused reflectance spectroscopy data. Cyclic voltammogram of both the solids showed reversible waves corresponding to Mo^{VI}/Mo^{V} electron process. The optical band gap energies of the solids showed slight difference on account of their difference in the nature of the ligands.

In chapter III, self-assembly of molybdate and phosphate precursors in the presence of zinc ions and organic ligands *viz.* benzimidazole (*bimi*), 4-aminopyridine (4-*ap*) and pyrazole (*pz*), has been carried out under hydrothermal condition. The crystallization of

Strandberg cluster based solids {H*bimi*}$_5$[$HP_2Mo_5O_{23}$].5H_2O, {H*bimi*}$_6$[$P_2Mo_5O_{23}$].H_2O, {4-H*ap*}$_4$[$H_2P_2Mo_5O_{23}$].2H_2O, {4-H*ap*}$_5$[$HP_2Mo_5O_{23}$] and {H*pz*}$_6${Zn(*pz*)$_4$(H_2O)$_2$} [{Zn(*pz*)$_2$$P_2Mo_5O_{23}$}$_2$].8$H_2O$ was observed. The chapter highlights the structural differences in the supramolecular isomers; and the effect of supramolecular isomerism and nature of ligands on the optical band gap energies (E_g) of the synthesized solids.

In chapter IV, an attempt was made to crystallize phosphorous and molybdenum precursors in the presence of $MCl_2.xH_2O$ (M = Co, Ni, Cu and Zn) with pyrazole to form PMO solids of varying dimensionality. The solids obtained were: {H*pz*}$_6${Zn(*pz*)$_4$(H_2O)$_2$}[{Zn(*pz*)$_2$$P_2Mo_5O_{23}$}$_2$].8$H_2O$**,** [{Cu(*pz*)$_4$}$_2$ {$H_2P_2Mo_5O_{23}$}].H_2O, {Ni(*pz*)$_4$}[{Ni(*pz*)$_4$}$_2${$H_2P_2Mo_5O_{23}$}]$_2$ [{Ni(*pz*)$_4$}{Ni(*pz*)$_4$ (H_2O)} {$HP_2Mo_5O_{23}$}]$_2$. 14H_2O, [Ni(*pz*)$_4$$Cl_2$], {*pz*}$_2$[{Co(*pz*)$_4$}$_5$ {$P_2Mo_5O_{23}$}$_2$].6H_2O and [{Cu(*pz*)$_2$}$_4$ {$CuMo_{12}O_{38}(OH)_2$}].8H_2O. Among these, the last solid is a rare example of copper based Keggin cluster. Except for this solid, which was synthesized using hydrothermal method; all other solids were obtained via solvent evaporation method. The magnetic properties of the solids were investigated using Guoy Balance.

In chapter V, synthesis, characterization and dye removal efficiency of ammonium phosphomolybdate (APM) which is a Keggin-type solid has been discussed. It was concluded that APM could be effectively used as an ion-exchanger to remove cationic dye-stuffs from aqueous solution. The dyes used for investigation were methylene blue, malachite green, methyl red and eosin. The influence of parameters such as nature of light, amount of APM, contact time and pH on dye removal efficiency was investigated.

In chapter VI, the synthesis and characterization of two composites of APM with polyaniline and poly (N-methylaniline), namely APM/PAni and APM/PNMAni respectively have been summarised. The difference in band gap energy in APM upon the

formation of the composite was investigated, and the capacity of these composites in the removal of hexavalent chromium from aqueous solution was explored. It was concluded that APM/PNMAni could effectively reduce harmful Cr(VI) to environmentally benign Cr(III).

Chapter VII concludes the entire work and emphasizes the future scopes of PMO based hybrid solids.

LIST OF ABBREVIATIONS

1.	APM	Ammonium phosphomolybdate
2.	APM/PAni	Ammonium phosphomolybdate/polyaniline composite
3.	APM/PNMAni	Ammonium phosphomolybdate/poly(N-methylaniline) composite
4.	APS	Ammonium persulphate
5.	BET	Brunauer-Emmett-Teller
6.	BVS	Bond valence sum
7.	CTAB	Cetyl trimethyl ammonium bromide
8.	CV	Cyclic voltammetry
9.	DDW	Double distilled water
10.	DMF	Dimethyl formamide
11.	DMSO	Dimethyl sulphoxide
12.	DPC	Diphenyl carbazide
13.	EDAX	Energy dispersive X-ray spectroscopy
14.	EY	Eosin
15.	FESEM	Field emission scanning electron microscope
16.	FTIR	Fourier Transform Infrared
17.	GCE	Glassy carbon electrode
18.	JCPDS	Joint committee on powder diffraction standards
19.	MB	Methylene blue
20.	MG	Malachite green
21.	MR	Methyl red

22. ORTEP	Oak ridge thermal ellipsoid plot
23. PAN	Polyacrylonitrile
24. PAni	Polyaniline
25. PMA	Phosphomolybdic acid
26. PMMA	Polymethylmathacrylate
27. PMO	Phosphomolybdate
28. PNMAni	Poly(N-methylaniline)
29. $\{P_2Mo_5\}$	$\{P_2Mo_5O_{23}\}^{6-}$
30. $\{PMo_{12}\}$	$\{PMo_{12}O_{40}\}^{3-}$
31. $\{P_4Mo_6\}$	$\{P_4Mo_6O_{31}\}^{12-}$
32. POM	Polyoxometalates
33. PXRD	Powder X-ray diffraction
34. rGO	Reduced graphene oxide
35. SEM	Scanning electron microscopy
36. TGA	Thermogravimetric analysis
37. TMC	Transition metal complex
38. UV-DRS	Ultraviolet-Diffused reflectance spectroscopy
39. UV-Vis	Ultraviolet-visible
40. 2*a*3*mp*	2-amino-3-methylpyridine
41. 2*a*4*mp*	2-amino-4-methylpyridine
42. *bimi*	Benzimidazole
43. 4-*ap*	4-aminopyridine
44. *pz*	Pyrazole

45. 0-D	Zero dimensional
46. 1-D	One dimensional
47. 2-D	Two dimensional
48. 3-D	Three dimensional

ABSTRACT

Polyoxometalate (POM) is an important class of early transition metal-oxygen clusters with plenteous intrinsic structures and widespread applications. Phosphomolybdate (PMO), a prominent sub-class of POMs, has been attracting the attention of researchers on account of their versatile building blocks and controllable architectures. Supramolecular self-assembly is a powerful tool to create PMO solids with attracting properties. Important factors affecting the self-assembly process are nature of organic moiety, temperature, pH of the medium and nature of metal ions. Owing to the controllable external factors, the self-assembly can lead to the formation of supramolecular aggregates with varying size and dimensionality such as one dimensional chain, two dimensional sheets and three dimensional networks. Moreover, nitrogen donor ligands and their pH related nature play a vital role in the crystal engineering. They have the capability to form complex with metal centres or undergo protonation. Recently a new trend of designing composite materials of PMOs with suitable substances like polymers has been observed.

In this thesis, various novel PMOs with varying structure and dimensionality have been synthesized. The characterization of the synthesized solids was done successfully by single crystal X-ray diffraction, powder X-ray diffraction, fourier transform infrared spectroscopy and thermo gravimetric analysis. The behavior and dynamics of these solids on account of their non-bonding interactions involved in the self-assembly process and affecting factors have been illustrated. Some predominant properties of the synthesized solids like optical band gap energy, magnetic properties and electrochemical properties were investigated. Ammonium phosphomolybdate (APM), a member of Keggin-type PMO was synthesized and characterized. Its ability to remove cationic dye-stuffs from aqueous solutions was explored. Two unique composites of APM with

polyaniline and poly(N-methylaniline) *viz*. APM/PAni and APM/PNMAni were synthesized and characterized. Moreover, APM/PNMAni composite was found as a good candidate to reduce environmental pollutant Cr(VI) to Cr(III) from contaminated aqueous solution.

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