Investigations of Hybrid Inorganic-Organic Network Solids

A Thesis Submitted for the Degree of

Doctor of Philosophy

By

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“Fraction Demands - Totality Supplies”

-Guru Vethathiri Maharishi.

Dedicated to
All My
Beloved Teachers!

DECLARATION

I hereby declare that the matter embodied in this thesis entitled "**Investigations of Hybrid Inorganic-Organic Network Solids**" is based on the work carried out by me in the ***Chemistry and Physics of Materials Unit***, **Jawaharlal Nehru Centre for Advanced Scientific Research**, Jakkur, Bangalore, India, under the supervision of **Professor C. N. R. Rao, FRS**.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigations. Any omission that might have occurred by oversight or error in judgement is regretted.

March 2008,

Bangalore (A. Thirumurugan)

CERTIFICATE

Certified that the work described in the thesis entitled "**Investigations of Hybrid Inorganic-Organic Network Solids**" is the result of investigations carried out by **Mr. A. Thirumurugan** in the ***Chemistry and Physics of Materials Unit***, **Jawaharlal Nehru Centre for Advanced Scientific Research**, Jakkur, Bangalore, under my supervision.

March, 2008

Bangalore

(Prof. C. N. R. Rao)

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Preface

Hybrid inorganic–organic network compounds constitute an important class of materials that have been studied extensively over the last few years due to their potential applications in catalysis, gas separation and storage. Other properties which draw attention to these materials include magnetic, optical and electronic properties. An effective and widely used strategy for the design of hybrid framework solids is based on the selection of metal and ligand geometries to produce desired network topologies. The mode of linkage and the dimensionality of the inorganic sub network, along with the size, geometry, chemical functionality and various coordinating modes of the linkers, provide excellent means of controlling and modulating the properties in these solids. In an attempt to understand these aspects and design hybrid frameworks with novel structural features and properties, hybrid dicarboxylates have been explored in this thesis in terms of dimensionality and extended inorganic connectivity. In pursuit of the above understanding, benzene-, cyclohexane- and aliphatic-dicarboxylic acids have been employed to synthesize hybrid inorganic-organic frameworks of di- and trivalent metal ions with or without chelating amines. To understand the process of formation of a three-dimensional zinc terephthalate, a systematic time and temperature dependent transformation study has been carried out. Investigations were also carried out to synthesize novel hybrid solids and nano materials by employing ionic liquids as solvents.

After providing an brief overview on hybrid inorganic-organic frameworks (Chapter 1), the thesis presents the results of the investigations of the hybrid benzenedicarboxylates (BDCs) of the three isomeric (1,2-, 1,3- and 1,4-) benzenedicarboxylic acids with divalent cations of Zn, Cd, Pb and trivalent cations of lanthanides (in Chapter 2). Several coordination polymers and the hybrids with extended inorganic connectivity of BDCs in different dimensionality have been prepared under hydrothermal conditions. Few of them have been doped Eu and Tb and they exhibit the lanthanide-centered red and green emission sensitized by the ligands at room temperature. The studies on zinc terephthalates show that a progressive transformation of a one-dimensional structure to a three-dimensional structure and the possible presence of a dimensional hierarchy.

Chapter 3 presents the results of the investigations of the hybrid cyclohexane and cyclohexenedicarboxylates (CHDCs and CHeDCs) of the three isomeric (1,2-, 1,3- and 1,4-) flexible cyclohexanedicarboxylic acids in different conformation with cations of Mn, Cd, Pb and La and 1,2-cyclohex(4)enedicarboxylic acid with Cd(II) cation. Several coordination polymers and the hybrids with extended inorganic connectivity in different dimensionality have been prepared under hydrothermal conditions.

Chapter 4 presents the results of the investigations of the hybrid aliphatic-dicarboxylates. These novel hybrid networks with extended inorganic connectivity, have been synthesized hydrothermally by employing single (homoleptic) and mixture (heteroleptic) of aliphatic dicarboxylicacids with the potentially lone pair active, flexible coordinating Pb(II) cation with larger ionic radii.

Chapter 5 presents the results of the investigations on a hybrid dihydroxybenzoate. A novel three-dimensional coordination network of lead 2,6-dihydroxybenzoate with (3,6) 3D net topology, has been synthesized and characterized.

Chapter 6 presents the results of the investigations on the exploration of ionic liquids as solvents to synthesize novel hybrid frameworks and nano materials. Ionic liquids are salts with low melting points ($<100^{o}C$), consisting of a bulky organic cation and an organic or inorganic anion. Two imidazolium bromoplumbates which exhibit unusual supramolecular organization with channel structures have been obtained by heating imidazolium bromide-based ionic liquids with lead (II) salts under ionothermal conditions. Nanocrystals, nanorods, nanowires and nanobelts of various elemental chalcogens and metal oxides have been synthesized by using imidazolium [BMIM]-based ionic liquids as solvents at 100 – 200 °C.

CONTENTS

Chapter 3. Hybrid Networks of Metal Cyclohexanedicarboxylates

Chapter 4. Hybrid Networks of Lead Aliphaticdicarboxylates with Extended Inorganic connectivity