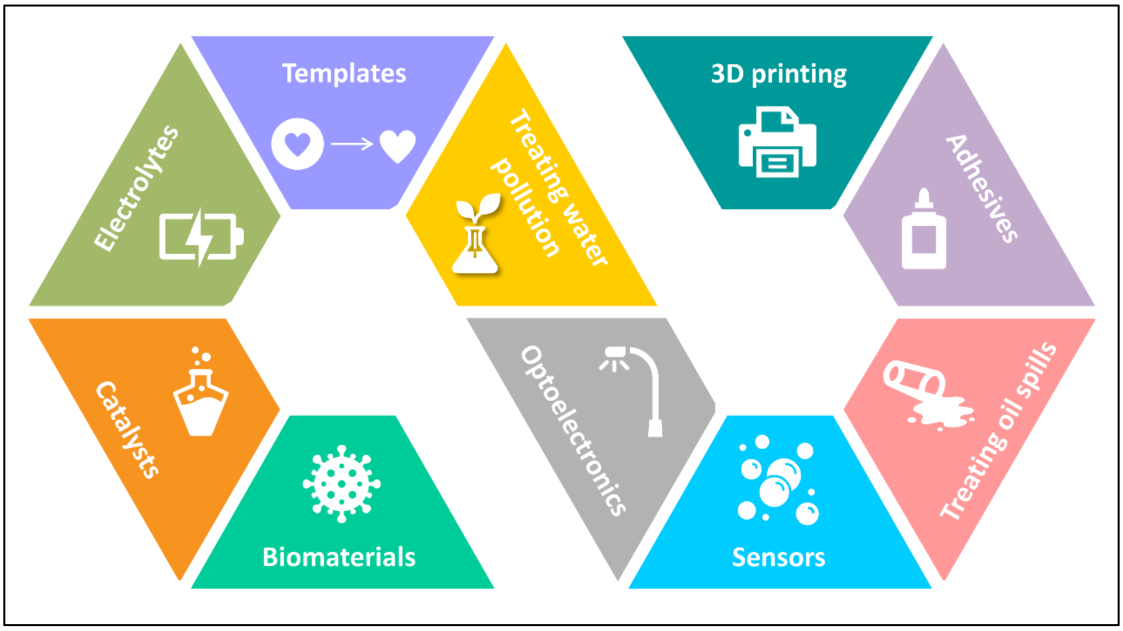
SYNOPSIS

of the thesis entitled

Design, Synthesis and Applications of Novel Supramolecular Assemblies



submitted to

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

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DOCTOR OF PHILOSOPHY

in

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by

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The thesis is presented in the form of following chapters –

Chapter 1

INTRODUCTION

Chapter 2

A combinatorial library of Memantine based salts – crystallography, Hirshfeld surfaces and dissolution studies

Chapter 3A

A series of pivalic acid based multi-component systems – gelation behavior, solvent parameter study and template directed nano particle synthesis

Chapter 3B

Probing the role of weak interactions on gelation behavior of *tert*-butylacetic acid based multi-component systems

Chapter 4A

A novel class of pivalamide based organogelators with potential applications in oil spill remediation and sequestration of dyes from water

Chapter 4B

Supramolecular assemblies based on *tert*-butylacetic acid with potential applications in Phase Selective Organo-Gelation (PSOG), dye absorption and sensing studies

Chapter 5

Syntheses, characterization and SOD *synzyme* activity of copper(II) complexes with bi-dentate pivalamide ligands – crystallography, DFT studies and DNA/BSA interactions

Chapter 1 – INTRODUCTION

Chapter 1 deals with the introduction of supramolecular chemistry, crystal engineering, role of non-covalent interactions (Figure 1), Hirshfeld surfaces and classification and characterization of Low Molecular mass Organo-Gelators (LMOGs) (Figure 2). The role of solvent parameters in controlling gelation behavior is discussed. The chapter focusses on the recent advancements made in the area of supramolecular gelation in the last five years.

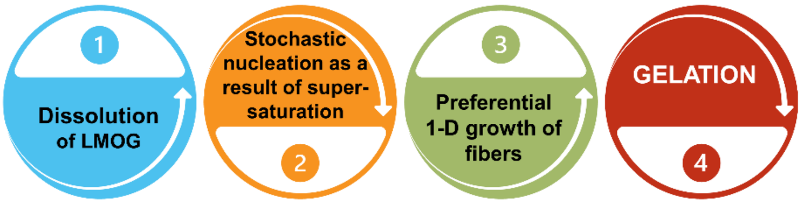

Figure 1 Preferential mechanism of gelation

This work is an effort to explore the presence of weak and highly directional non-covalent interactions such as hydrogen bonding, π-π, C-H…π interactions, etc. and relatively stronger and not-so-directional interactions such as electrostatic interactions to generate interesting supramolecular architectures and establish their role in modification of drug formulations and governing supramolecular gelation/non-gelation behavior by investigating structure–property relationship; to investigate the applications of supramolecular gels in generating inorganic nanostructures, oil spill remediation, dye uptake, etc.

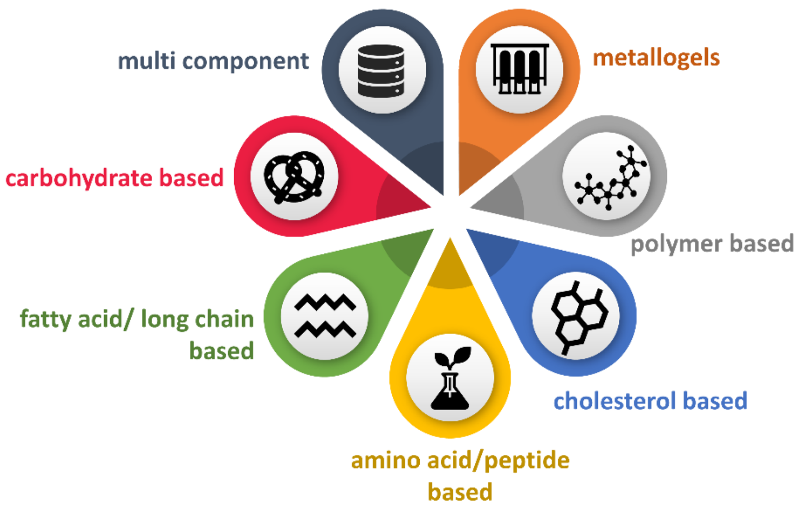

Figure 2 Classification of LMOGs

Chapter 2 – A combinatorial library of Memantine based salts – crystallography, Hirshfeld surfaces and dissolution studies

Chapter 2 discusses the synthesis and characterization of memantine (MEM) based salts using a combinatorial library approach. The efficiency of pharmaceutical cocrystals and their design based on crystal engineering and supramolecular synthon approach is discussed in detail (Figure 3). Various mono-, di- and tri-carboxylic acids with aliphatic and aromatic backbones were employed in the study. The salts synthesized were explored for their propensity to form various supramolecular synthons, as primary ammonium monocarboxylate (PAM) which can be easily extended to 2D by the presence of additional carboxylic acid functionality. A comparative study of weak non-covalent interactions present in the parent compound MEM.HCl and newly synthesized salts of memantine was carried out in order to attain better understanding of the trends obtained from the dissolution studies of the newly synthesized MEM salts. Intermolecular interaction energies of salts were also measured with HF/3-21G basis sets to evaluate the contribution of stabilizing and destabilizing interactions in the crystal structures.

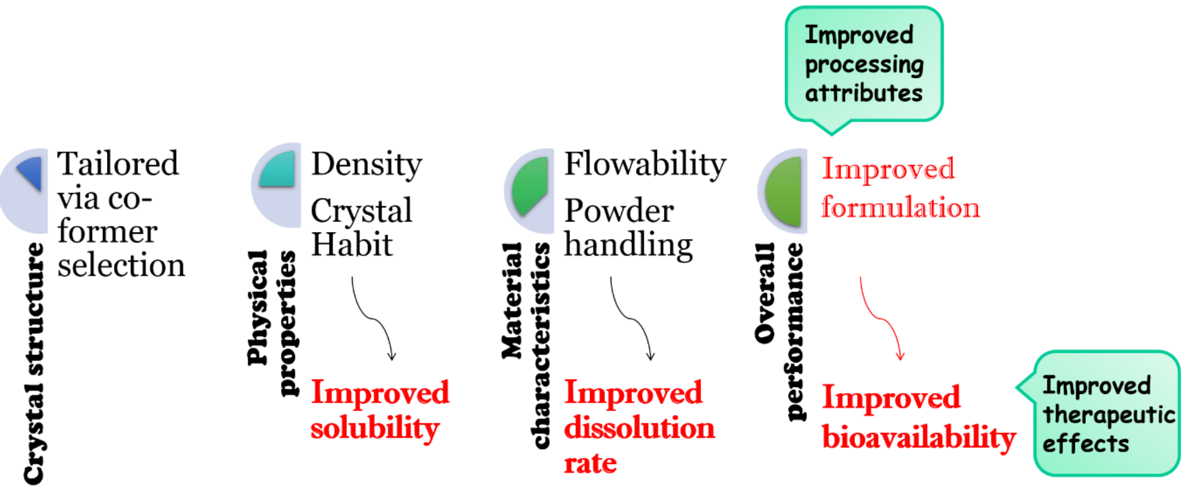

Figure 3 Rational designing of pharmaceutical co-crystals using crystal engineering

Chapter 3A – A series of pivalic acid based multi-component systems – gelation behavior, solvent parameter study and template directed nano particle synthesis

Chapter 3A deals the synthesis of organic salts based on pivalic acid and primary amines (with aliphatic, alicyclic, and aromatic backbones). 10 out of 13 salts turned out to be organogelators. Single crystal studies were carried out to understand the hydrogen bonding patterns and to probe the mechanism of supramolecular gelation/non-gelation from crystal engineering approach. The role of solvent parameters such as dielectric constant, Hildebrand parameter, Hansen parameters, Kamlet-Taft parameters, etc. was also investigated in driving the gelation behavior. One of the gelators displayed well-defined rectangular pores in its fibers, which was utilized to serve as template for the synthesis of silver nanoparticles (Figure 4).

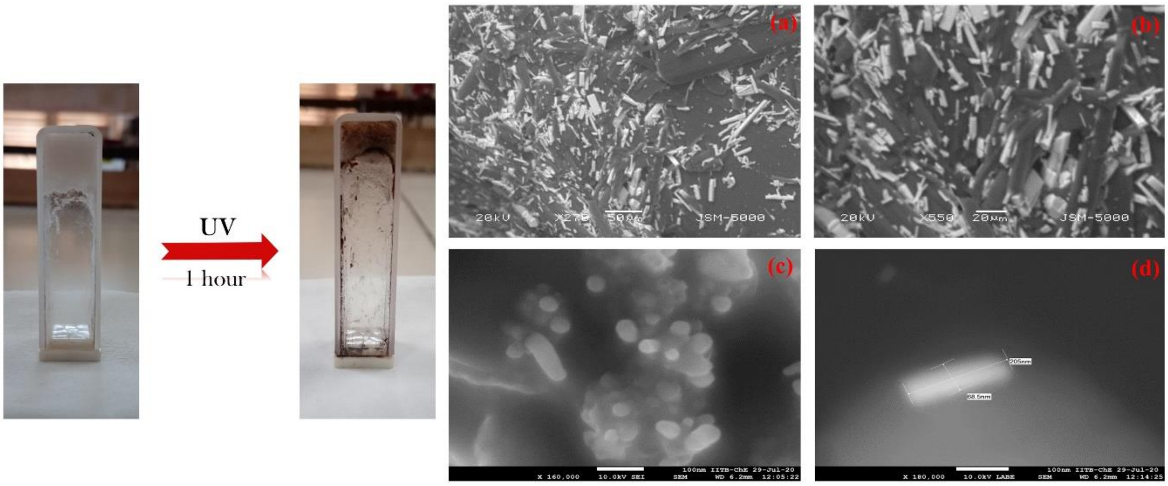

Figure 4 Synthesis and morphology of silver nano particles

Chapter 3B – Probing the role of weak interactions on gelation behavior of *tert*-butylacetic acid based multi-component systems

Chapter 3B discusses the synthesis and characterization of *tert*-butylacetic acid based salts along with the same set of primary amines as in Chapter 3A. All the salts were tested for their gelation behavior in various types of solvents. The behavior of pivalic acid based salts and *tert*-butylacetic acid based salts to form gels was assessed to identify better class of gelators and probable driving forces behind causing gelation.

Chapter 4A – A novel class of pivalamide based organogelators with potential applications in oil spill remediation and sequestration of dyes from water

Chapter 4A describes the syntheses and characterization of pivalamide based compounds having 3 parts - 1. structural moiety which can promote van der Waals/π-π interactions (long-chain aliphatic/ aromatic compounds), 2. directional hydrogen bonding linker (amide) and 3. bulky end group (*tert*-butyl). Six new gelators were discovered which could congeal alkane homologues (n>5 carbon atoms), diesel, engine oil, silicone oil, cooking oil, etc. under the effect of strong sunlight, UV light and ultrasonication. These compounds were tested for their ability to selectively congeal oil from oil-water systems at room temperature, in various forms (powder as well in solution form using various solvents). They were also employed for removing dyes present in aqueous solutions, which can contribute to tackle water pollution (Figure 5).

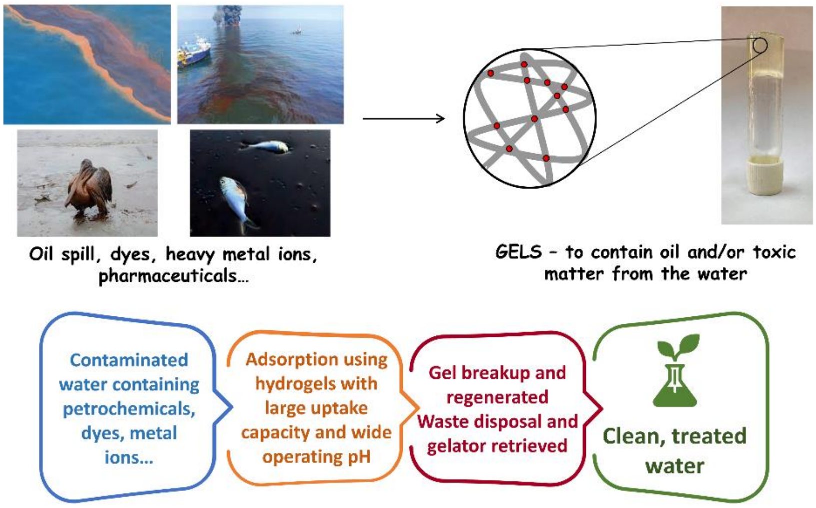

Figure 5 Organogels for oil spill remediation and treatment of water pollution

Chapter 4B – Supramolecular assemblies based on *tert*-butylacetic acid with potential applications in Phase Selective Organo-Gelation (PSOG), dye absorption and sensing studies

Chapter 4B deals with syntheses and characterization of *tert*-butylacetic acid based amides, using the same set of amines as in Chapter 4A. Their gelation abilities were compared with those of the compounds prepared in Chapter 4A. These compounds were explored for their phase selective organo-gelation behavior, dye removal and heavy metal sensing studies.

Chapter 5 – Syntheses, characterization and SOD *synzyme* activity of copper(II) complexes with bi-dentate pivalamide ligands – crystallography, DFT studies and DNA/BSA interactions

Chapter 5 describes synthesis of pivalic acid-based amides containing heterocyclic (thiazole and imidazole based) backbones. These compounds were utilized for the synthesis of mononuclear copper metal complexes. They were characterized using single crystal X-ray studies, Hirshfeld surface analysis, computational studies, ESI-mass spectrometry, UV-vis and ESR spectroscopy. These complexes were also exploited for their antioxidant activity, DNA cleavage, BSA binding and DNA binding abilities (Figure 6).

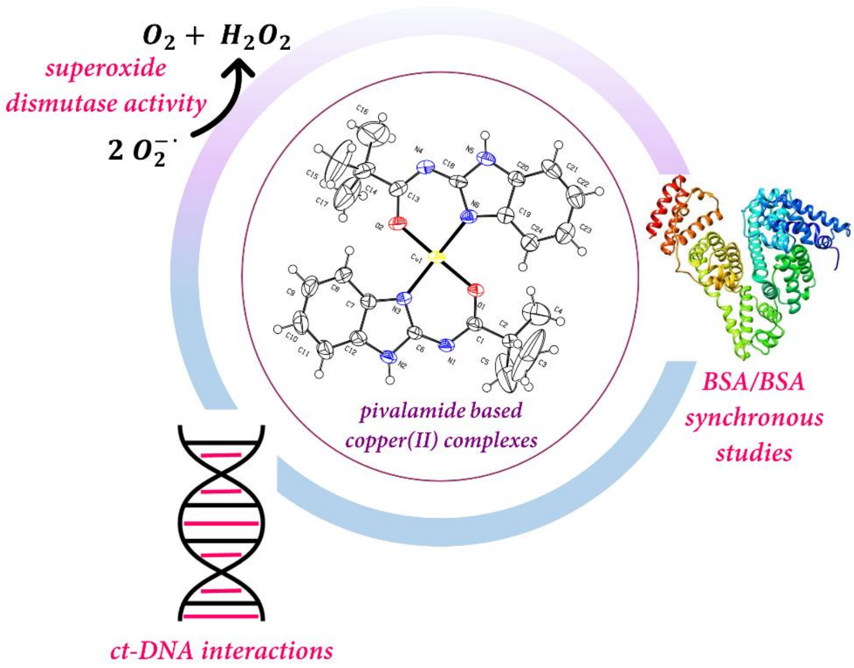

Figure 6 Biomimetic activities of the complexes synthesized