Abstract

Ionic liquids, generally considered as one of the 'greener' alternatives to volatile organic solvents, are molten organic salts that exist below 100 °C [1-3]. They are primarily composed of organic cations such as imidazolium, pyridinium, ammonium, sulfonium, phosphonium cations etc. and organic or inorganic anions such as acetate, triflate, chloride, carboxylate, hydroxide, nitrate, tetrafluoroborate, hexafluorophosphate etc. These cations as well as anions mainly govern the unique physicochemical properties of ionic liquids like moderate viscosity, high polarity, non-flammability, low vapor pressure, low melting point, high electrical conductivity, miscibility with various solvents, ability to dissolve organic/inorganic/polymeric materials etc. [4]. For this reason, ionic liquids are often termed as 'designer solvents' as their properties can be modified by altering their constituent cations/anions [5]. Ionic liquids, that are found in liquid state at ambient temperature, are known as 'room temperature ionic liquids' (RTILs) [6]. Specific functional groups such as -COOH, -SO_3H, OH, -NH_2 etc. are introduced to the cation or anion or both the ions to develop 'task-specific ionic liquids' [7]. These functional groups enhance the properties such as acidity/basicity, redox behaviour, hydrophilicity/hydrophobicity, thermal stability, semiconducting behaviour etc. that are required for a certain task.

Ionic liquids/organic salts sometimes contain main group metals, transition metals or rare earth metals in their complex anionic speciation to generate organic-inorganic hybrids such as halometallate ionic liquids/organic salts. They are fundamentally distinguished as Lewis acidic ionic liquids and are known to perform better in acidic reactions as compared to the conventional ionic liquids [8]. Due to the Lewis acidic nature, halometallate organic salts are utilized in other catalytic reactions like alcoholysis of polycarbonates, hydrochlorination of acetylene, hydrosilylation of olefins, Friedel-Crafts benzylation to synthesize diphenylmethane and derivatives, Knoevenagel condensation to prepare electrophilic alkenes, deep oxidative desulfurization of fuels etc. [9]. When H-donor functional groups like -COOH, -SO_3H etc. are attached to the cations of halometallate organic salts, Brønsted-Lewis acidic organic salts are formed. Their acidity is further increased, owing to the presence of both proton donor and electron acceptor groups in such dual Brønsted-Lewis acidic halometallate ILs. They are utilized as acid catalysts in catalytic reactions such as the conversion of chitosan to 5-

hydroxymethylfurfural in water medium, conversion of cellulose into 5-hydroxymethylfurfural, cellulose conversion to levulinic acid, alkylation of isobutane/isobutene, oxidative desulfurization of fuels etc. [10]. The biologically as well as pharmaceutically important N-heterocycles, quinazolines and quinazoline derivatives, have been produced by using various methods with or without catalysts or solvents [11]. However, most of these reactions involved several issues such as the use of expensive catalysts, excess amounts of oxidants, harsh conditions, longer reaction time, difficulty in catalyst separation, no recyclability etc. [12]. By considering the enhanced acidity of Brønsted-Lewis acidic halometallate ILs, we intended to develop a series of N-sulfonic acid functionalized piperazinium-based chlorometallate salts of transition metals as heterogeneous catalysts to synthesize 1,2-dihydroquinazoline derivatives in a one-pot three-component method under mild conditions.

Similarly, selective oxidation of alcohols to carbonyl compounds and selective oxidation of organic sulfides to sulfoxides are considered as important transformations chemically as well as biologically [13, 14]. When these oxidation reactions are carried out using $KMnO_4$ as an oxidant, over-oxidized products are obtained under harsh reaction conditions, apart from the solubility issue of organic substrates in aqueous $KMnO_4$ and gradual thermodynamic instability of $KMnO_4$ in water [15]. Although modifications of $KMnO_4$ are done by using solid support etc. to increase the product selectivity in alcohol oxidation and sulfide oxidation reactions, problems like over-oxidation as well as excess use of $KMnO_4$/solid support reagents continued [16]. In this regard, a category of fascinating organic-inorganic hybrid salt was developed by introducing MnO_4^- anion of potassium permanganate to the ammonium/phosphonium cations with varying alkyl side chains without any functional groups attached to them [17]. These organic-inorganic hybrid permanganate salts exhibited commendable performances in oxidation as well as dihydroxylation reactions, by enhancing unique characteristics while lowering the drawbacks of individual units [17]. However, due to insufficient thermal stability, low decomposition temperature, tendency to undergo self-oxidation etc. behaviour, their applicability as oxidants is still restricted [18]. In this context, thermally stable N-sulfonic acid functionalized ammonium and imidazolium-based permanganate hybrids could be developed for potential uses as recyclable internal oxidative catalysts for conversion of alcohols to keto compounds and selective oxidation of organic sulfides to sulfoxides in aqueous acidic solutions under mild conditions.

Again, the side-effects of using and discarding organic pollutants in nature is well-known [19]. To get rid of these hazardous effects, easy and effective way of organic pollutants degradation is much desired. Among the advanced oxidative processes, extensive uses of ZnO semiconductor are observed, owing to its unique beneficial characteristics [20]. However, several disadvantages such as rapid recombination of electron/hole pairs, inability to absorb visible light, deactivation, difficulty in reuse etc. are associated with ZnO semiconductor [21]. To overcome these problems, Ag containing ZnO nanoparticles have been developed by various methods [22]. On the other hand, ionic liquids/organic salts are noted to act as stabilizing agents, reaction templates, reaction medium, shape detector etc. in the synthesis of nanoparticles/nanocomposites [23-25]. Considering the effects of ionic liquids/organic salts on the growth of stable metal nanoparticles, Ag and Ag_2O containing ZnO nanoheterocomposites could be fabricated in sulfonic acid functionalized cyclic/acyclic ammonium chloride salts to use them as photocatalysts in the degradation of organic dyes under visible light.

The works included in this thesis are mainly the development of transition-metal based functionalized organic salts and Brønsted acidic organic salts assisted nanomaterial synthesis and their uses in the synthesis of 1,2-dihydroquinazoline derivatives, selective oxidation of primary/secondary benzyl alcohols to carbonyl compounds, selective oxidation of organic sulfides to sulfoxides and the degradation of organic dyes.

Proposed objectives:

(1) Development of N,N'-disulfopiperazinium chlorometallates of Fe(III), Ni(II) and Co(II) as hybrid heterogenous catalysts for the synthesis of 1,2-dihydroquinazoline derivatives.

(2) Development of permanganate based functionalized organic-inorganic hybrid as an internal oxidative catalyst for selective oxidation of primary/secondary alcohols.

(3) Development of sulfonic acid functionalized ammonium-based permanganate hybrid as internal oxidative catalyst for selective conversion of organic sulfides to sulfoxides.

(4) Fabrication of nano-heterostructured composites of $Ag/Ag_2O/ZnO$ by sulfonic acid functionalized organic salts for photocatalytic degradation of organic dyes under visible light.

Plan of work:

1. Designing and characterization of Brønsted-Lewis acidic N,N'-disulfopiperazinium chlorometallates of Fe(III), Ni(II) and Co(II) hybrid salts.
2. Exploration of the chlorometallate salts as heterogeneous catalysts in the one-pot three component synthesis of 1,2-dihydroquinazoline derivatives.
3. Designing and characterization of organic-inorganic hybrid permanganate salt from 2-methyl-1,3-disulfoimidazolium chloride and $KMnO_4$.
4. Exploration of the permanganate salt as internal oxidative catalyst in the selective oxidation of benzyl alcohols to carbonyl compounds.
5. Designing and characterization of two organic-inorganic hybrid permanganate salts from N,N'-diethyldisulfoammonium chloride and 1,4-disulfopiperazinium chloride with $KMnO_4$.
6. Exploration of the permanganate salts as internal oxidative catalysts in the selective oxidation of organic sulfides to sulfoxides.
7. Development and characterization of $Ag/Ag_2O/ZnO$ nanocomposites in presence of 1,4-disulfopiperazinium chloride and 2-methyl-1,2-disulfoimidazolium chloride organic salts.
8. Exploration of photocatalytic activities of the above-mentioned nanocomposites in the degradation of organic dyes under visible light.

Outline of this thesis:

This thesis is divided into **six** chapters. The first chapter gives a general introduction about ionic liquids/organic salts and the literature surveyed for the thesis works. **Chapter 2-5** contain the work done to develop the ionic liquid/organic salt based/assisted materials and their applications. **Chapter 6** gives a summary of the work done in **Chapter 2-5** and the future scopes.

Chapter 1:

It is divided into two parts, as **Chapter 1A** and **Chapter 1B**.

Chapter 1A: General Introduction

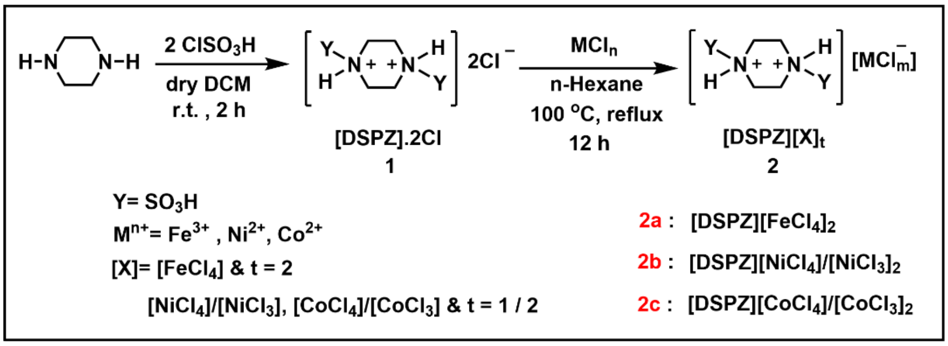
This chapter provides a relevant overview of ionic liquids and a general introduction to their various classes. The applicability of ILs/organic salts in the synthesis of metal nanoparticles are also briefly discussed. The next section illustrates the importance of halometallate organic salts and admissible literature on the synthesis of quinazolines as well as their derivatives to understand the scope of using halometallate organic salts in the synthesis of quinazolines. The significance of organic-inorganic hybrids of permanganates along with the literature on controlled oxidation of alcohols/organic sulfides using permanganate hybrid salts are also concisely discussed. The last section describes the backgrounds of organic pollutants decomposition by Ag based ZnO nanocomposites.

Chapter 1B: Materials & Methods

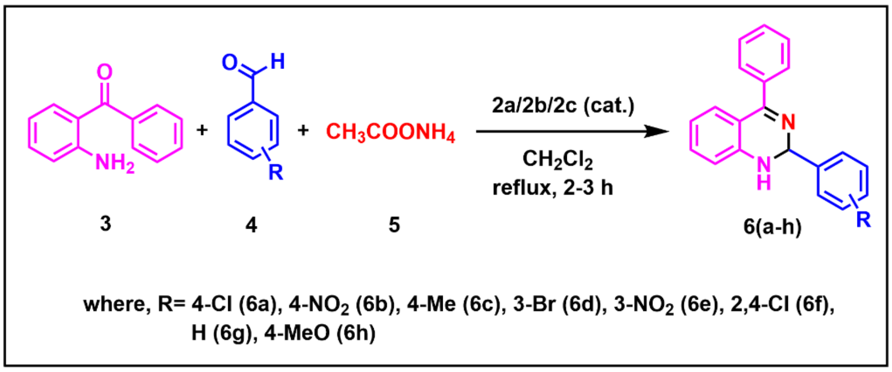
This chapter gives an overview of the materials and methods used while carrying out the works related to this thesis. It includes a brief description of the analytical techniques used in the characterization of synthesized materials and organic products formed.

Chapter 2: Investigation of N,N'-Disulfopiperazinium Chlorometallates as Hybrid Catalysts for the Synthesis of 1,2-Dihydroquinazoline Derivatives

This chapter focuses on developing three chlorometallate organic salts of Fe(III), Ni(II) and Co(III) as Brønsted-Lewis acid catalysts in the synthesis of 1,2-dihydroquinazoline derivatives (**Scheme 2.1**). In these hybrids, Fe(III) metal exists as $FeCl_4^-$, while Ni(II) and Co(II) metal exist in equilibrium speciation of $NiCl_4^{2-}/NiCl_3^-$ and $CoCl_4^{2-}/CoCl_3^-$. The synthesized hybrid salts are thermally more stable as compared to the parent organic salt due to the presence of anionic metal halide complexes and sulfonic acid group attached to the piperazinium cations, enabling electrostatic interactions among the constituent ions. Among them, sulfonic acid functionalized piperazinium hybrid with $FeCl_4^-$ anion is found to possess highest Brønsted acidity. Due to the synergistic Brønsted-Lewis acidity, the chlorometallate hybrids are used as heterogeneous acidic catalysts in the three-component one-pot synthesis of 1,2-dihydroquinazoline derivatives (**Scheme 2.2**). Various advantages like thermal stability of catalysts, ease of catalyst separation from the reaction mixture, catalyst recyclability, mild reaction conditions with good product yields etc. indicate that a favourable method can be developed with these chlorometallate hybrid organic salts to achieve the first objective.



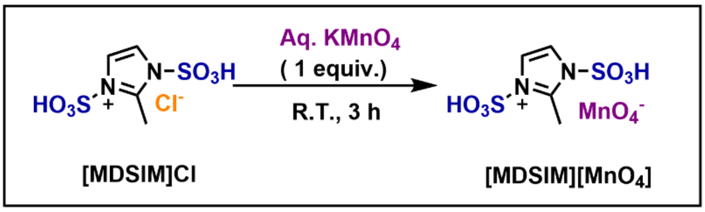
Scheme 2.1: Synthesis of dicationic halometallate hybrids of piperazinium cations.



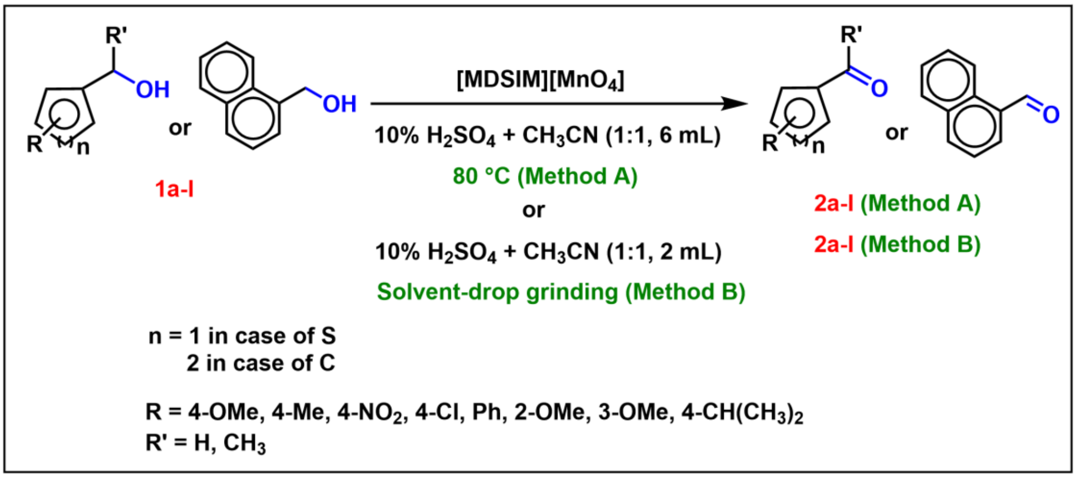
Scheme 2.2: Synthesis of 1,2-dihydroquinazoline products via a three-component reaction.

Chapter 3: Functionalized Imidazolium-Based Permanganate Organic-Inorganic Hybrid as Internal Oxidative Catalyst for Controlled Oxidation of Benzyl Alcohols

In this chapter, an N-sulfonic acid functionalized imidazolium cation-based permanganate salt [MDSIM][MnO_4] is prepared at room temperature through anion-exchange reaction between the parent ionic liquid [MDSIM]Cl and $KMnO_4$ (**Scheme 3.1**). Unlike most of the reported permanganate hybrid salts of ammonium cation, [MDSIM][MnO_4] is found to be thermally stable, do not explode at high temperature and can be stored at room temperature for prolonged duration. The inclusion of MnO_4^- anion in [MDSIM][MnO_4] hybrid is confirmed by the presence of characteristic peaks of MnO_4^- anion in PXRD, Raman and UV-vis DRS spectra of the hybrid. Two methods of alcohol oxidation (**Method A & Method B, Scheme 3.2**) are developed where [MDSIM][MnO_4] acts as an internal oxidative catalyst in the controlled conversion of alcohols to carbonyl compounds in acidic condition which acts as a co-catalyst. Using **Method A**, the oxidation is done in a 1:1 mixture solution of 10% aqueous H_2SO_4 and acetonitrile solution at 80 ºC which generates satisfactory yields of carbonyl compounds, while **Method B** requires solvent-assisted grinding, using the same mixture solution, for selective conversion of alcohol at room temperature following a ‘green approach’, although generating comparatively low product yields. The highest product yields are obtained with alcohols with electron-donating substituents at *para*-position and smaller size. Theoretical calculations reveal the presence of various interactions among the constituents of [MDSIM][MnO_4] and favor the proposed mechanism as thermodynamically feasible. The fabrication of the stable hybrid permanganate salt, selective conversion of alcohols to carbonyls without over-oxidation, no need for concentrated acids or external oxidizing agents, catalyst recyclability, practicing ‘green approach’ etc. reasons indicate that the second objective can be realized effectively.



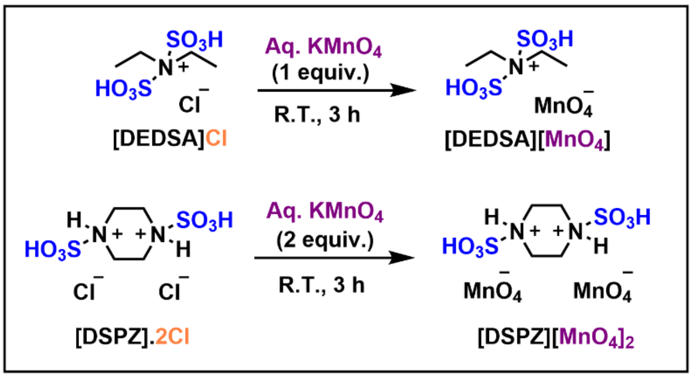
Scheme 3.1: Synthesis of hybrid permanganate salt of sulfonic acid functionalized 2-methylimidazolium cation.



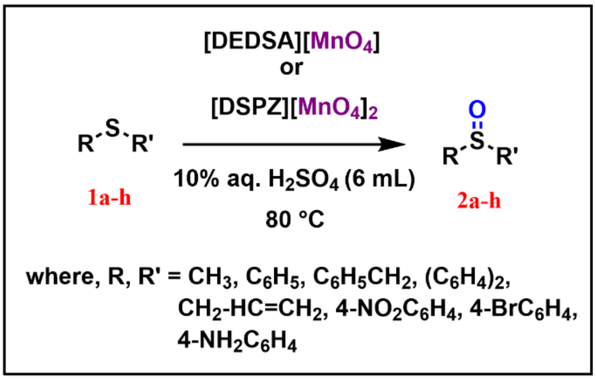
Scheme 3.2: Selective oxidation of aromatic alcohols by the synthesized permanganate salt under heating conditions (**Method A**) and solvent-drop grinding conditions (**Method B**).

Chapter 4: Functionalized Ammonium-Based Permanganate Hybrids as Sustainable Oxidative Catalysts for Selective Conversion of Organic Sulfides to Sulfoxides

Hybrid salts of permanganate anion with other ammonium cationic moieties such as N,N'-diethyldisulfoammonium ($[DEDSA]^+$) and 1,4-disulfopiperazinium ($[DSPZ]^{2+}$) are developed in this chapter (**Scheme 4.1**). The monocationic hybrid $[DEDSA][MnO_4]$ and the dicationic hybrid $[DSPZ][MnO_4]_2$ exhibit extensive thermal stability and other properties like those of $[MDSIM][MnO_4]$. The inclusion of MnO_4^- anion in $[DEDSA][MnO_4]$ and $[DSPZ][MnO_4]_2$ hybrids is confirmed by the presence of characteristic peaks of MnO_4^- anion in PXRD, Raman and UV-vis DRS spectra of the hybrids. Catalytic amounts of these hybrid salts can selectively oxidize organic sulfides to sulfoxides in water in the presence of a diluted acidic co-catalyst (**Scheme 4.2**). In this method, less bulky organic sulfides are converted into sulfoxides within a short period of time, as compared to the bulkier ones. This method also displays chemoselectivity by oxidizing the sulfide group, without disturbing the allylic group. When the three synthesized permanganate hybrid salts (from **Chapter 3** as well as **Chapter 4**) are compared, less sterically hindered $[DEDSA][MnO_4]$ and $[MDSIM][MnO_4]$ salts are observed to portray excellent catalytic/oxidizing efficiency than the sterically crowded dicationic $[DSPZ][MnO_4]_2$. This method involves advantages like short reaction time, no additional oxidants, chemoselectivity by catalysts, and recyclability of catalyst etc., which make it a reliable sustainable oxidative approach to achieve the third objective.



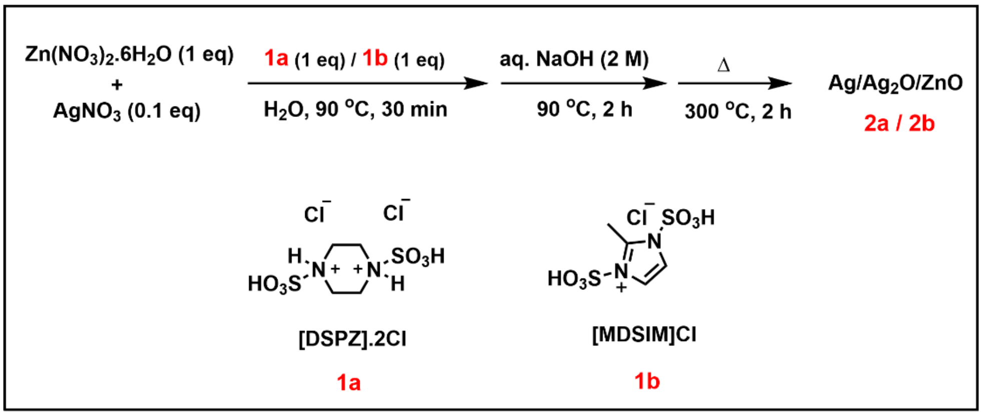
Scheme 4.1: Synthesis of permanganate hybrids of -SO_3H functionalized diethylammonium/piperazinium cations.



Scheme 4.2: Selective oxidation of sulfides to sulfoxides by the permanganate hybrids.

Chapter 5: Fabrication of Nano-heterostructured Composites of Ag/Ag_2O/ZnO by -SO_3H Functionalized Organic Salts for Photocatalytic Study of Organic Dyes

This chapter involves fabrication of two Ag based ZnO nanocomposites from $Zn(NO_3)_2.6H_2O$ and $AgNO_3$ in aqueous solution of two Brønsted acidic organic salts i.e. 1,4-disulfopiperazine-1,4-diium chloride ([DSPZ].2Cl]) and 2-methyl-1,3-disulfoimidazolium chloride ([MDSIM]Cl) by precipitation method (**Scheme 5.1**). In this method, 10% $AgNO_3$ is taken with reference to $Zn(NO_3)_2.6H_2O$ to prepare Ag/Ag_2O/ZnO nanoheterocomposites, where the organic salts are utilized as reaction templates and stabilizing agents for the growth of nanoparticles. The presence of Ag, Ag_2O and ZnO in the nanocomposites is confirmed by FT-IR, EDX, PXRD, Raman, XPS and UV-vis DRS spectra. SEM images display the capsule-like structure and sheet-like structure in the two nanocomposites. TEM images suggest that one Ag/Ag_2O/ZnO nanocomposite is of capsule-like structure with 59.7 nm average size having Ag positioned as a cap on the ZnO nanocapsules with average size of 27.56 nm, while the other Ag/Ag_2O/ZnO nanocomposite is of sheet-like structure with 191.17 nm average size having spherical Ag nanoparticles with an average size of 22.34 nm scattered over the ZnO nanosheet layer. The BET isotherm plots indicate slight differences in specific surface area values of the two nanocomposites. Tauc plots give bandgap parameters of 1.39 eV and 1.43 eV for the two nanocomposites, which are much lower than the 3.3 eV bandgap for pristine ZnO. Based on such properties, the synthesized nanocomposites are used as photocatalysts in the degradation of organic dyes under solar light. A 15 mg amount of both the photocatalysts are capable of decomposing >95% methylene blue dye at pH 10. The catalysts show better activity under basic environment and visible light. Degradation of the cationic methylene blue dye mixed with other anionic/cationic (methyl orange/crystal violet) dyes is also accomplished under basic pH. In this degradation process, superoxide radical anion along with electrons are found to be the reactive oxidizing species. The catalysts also show recyclable nature in further dye degradation cycles. Therefore, this method proves to be beneficial to accomplish the 4th objective of this thesis.



Scheme 5.1: Synthesis of Ag/Ag_2O/ZnO nanocomposites (**2a** and **2b**) from the parent organic salts.

Chapter 6: Conclusion & Future scopes

This chapter discusses the findings of each chapter in the thesis. The modifications of ionic liquids/organic salts done during the thesis work are briefly discussed, along with their applications in various catalytic reactions. This chapter also discusses the work that can be done in future as the extension of the work involved in this thesis.

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Keywords: *Ionic liquids, Task-specific ionic liquids (TSILs), Halometallate organic salts, Brønsted-Lewis acidic ionic liquids (BAILs), Hammett acidity, Lewis acidity, Dual Brønsted-Lewis acidity, Multicomponent reaction, 1,2-dihydroquinazolines, Heterogeneous catalysis, 2-methyl-1,3-disulfoimidazolium cation, Organic-inorganic hybrid, Sulfonic acid functionalized organic salt, Permanganate hybrid salt, Internal oxidative catalyst, Benzyl alcohol oxidation, Selective oxidation, Green oxidation, Solvent-drop grinding, Carbonyl product, Homogeneous catalysis, N,N'-diethyldisulfoammonium cation, 1,4-Disulfopiperazinium cation, Oxidation of organic sulfides, Sulfoxides, Ag containing ZnO nanocomposite, Nanoheterostructure, Photocatalyst, Dye degradation, Mixed dye degradation, Recyclable catalyst.*