Chapter 1A

General Introduction

1A.1. Introduction

Over the past decades, volatile organic solvents have been known to cause environmental destruction on air, water and soil and thereby corrupt the health of living things due to their toxic or carcinogenic nature. In this regard, ionic liquids (ILs) have come to light as a comparatively gentler alternative to the volatile organic solvents [1, 2]. ILs are molten organic salts having a melting point below 100 °C [3]. Typically, ILs are composed of organic cations in association with organic or inorganic anions. Examples of organic cations include imidazolium, pyridinium, ammonium, sulfonium, phosphonium cations etc., which make sufficient electrostatic interactions with varied organic/inorganic counterions like acetate, triflate, chloride, carboxylate, hydroxide, nitrate, tetrafluoroborate, hexafluorophosphate etc. (**Fig. 1A.1**). They possess unique physicochemical properties such as 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]. The ILs that are liquid at room temperature, generally called room temperature ionic liquids (RTILs) [5], often provide a wide range of liquid state up to a high degree of temperature. Such properties have increased the desirability of ILs compared to conventional volatile organic solvents in many physical as well as chemical procedures. By varying their constituent ions, the ILs of desired specific physical/chemical properties could be achieved, for which they are also known as 'designer solvents' [6].

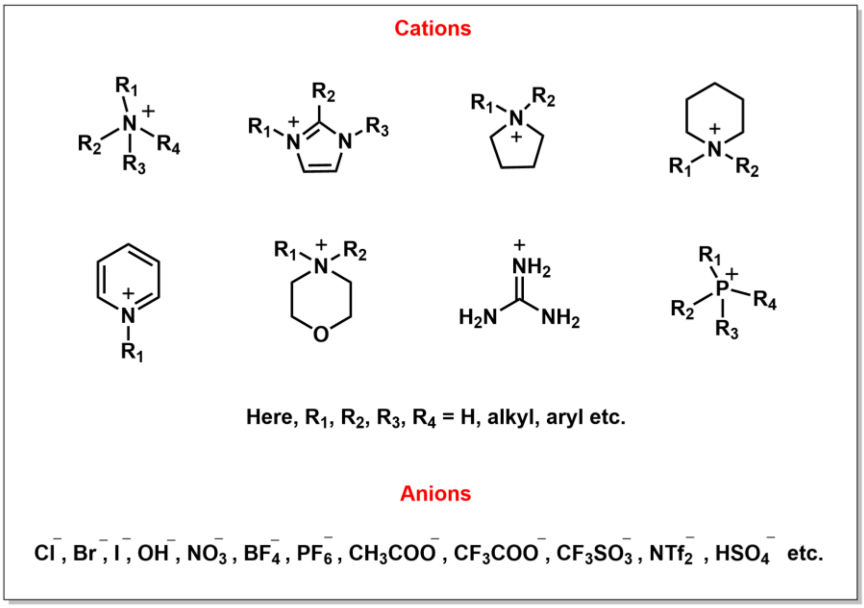


Fig. 1A.1: Common cations and anions that constitute ionic liquids.

1A.2. Functionalized ionic liquids/organic salts and their significance

The simplest description of salt expresses a pair of cation and anion together, where the nature of constituent ions may be either organic or inorganic or a mixture of both. ILs are organic salts that exist in molten state below 100 °C. The physicochemical properties of ILs/organic salts depend on the nature of constituent ions. With variation of the ion-pair compositions in ILs, one can 'tune' their physical properties like melting point, viscosity, polarity, hydrophilicity/hydrophobicity, surface tension, conductivity, density, water stability, thermal stability etc. The chemical reactivity of ILs/organic salts can be altered by introducing additional functional groups either to the cation or anion or both the ions. They engage in numerous chemical reactions, which are regulated by the type of functional groups retained in the constituent ions of organic salts. Based on the presence of acidic sites or basic groups in ILs, they are typically classified as Brønsted/Lewis acidic or sometimes dual Brønsted-Lewis acidic ILs and basic ILs. These modifications in conjunction gave rise to an interesting sub-class of ILs, which is called the 'task-specific ionic liquids' (TSILs). This includes introducing specific functional groups such as sulfonic acid, carboxylic acid, hydroxyl, amino, thiol, thiourea etc. into the ions of ILs through covalent interactions [7], which modify certain properties of the ILs such as acidity, basicity, hydrophilic/hydrophobic nature, miscibility with different solvents, thermal stability and moisture sensitivity etc. Furthermore, the incorporation of metal-based complex anions into the ILs provides an approach for transfer of metallic properties to the organic salt which include Lewis acidity, semiconductor behavior, redox properties, magnetic properties etc. [8]. Thereby, these task-specific organic salts have found extensive applications in the fields of catalysis, electrochemistry, organic and inorganic synthesis, magnetism and luminescence, gas absorption, analysis, industrial purpose etc. [9, 10]. In 2015, Li and co-workers synthesized a series of functionalized ILs containing -COOH, $-NH_2$, $-SO_3H$ and -OH groups in pyridinium based ILs and conducted density functional theory (DFT) investigation to study the catalytic efficiency of the functionalized ILs on carbon dioxide fixation with epoxides [11]. Chatterjee *et al.* prepared a thiourea functionalized imidazolium based RTIL and used it to increase functioning of Lithium-ion batteries [12]. Yeon *et al.* synthesized four hydroxyl-functionalized imidazolium and morpholinium based RTILs and studied their physical as well as electrochemical properties to use them as electrolytes [13]. Barsanti and the group investigated the properties of functionalized ILs of phosphonium cation and utilized them to extract various metals from water [14]. Some reported task-specific functionalized organic salts are mentioned in **Fig. 1A.2**.

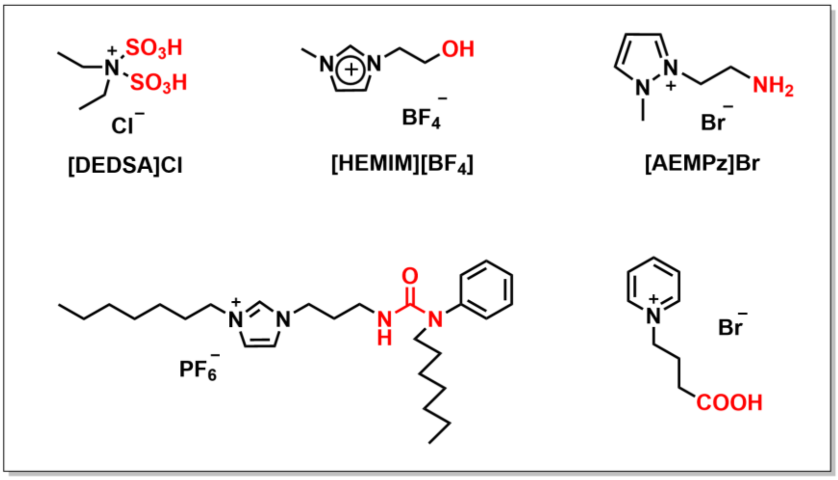


Fig. 1A.2: Some reported task-specific functionalized organic salts.

1A.3. Organic salts with metals

The existence of metal centered complex anionic speciation within the organic salts promotes their extensive uses in catalysis, electrochemistry, sensing, redox reactions, nanomaterial synthesis etc. [15]. The metals that are usually observed as complex anionic speciation in such organic salts are transition metals, main group metals and rare earth metals. However, the organic salts that contain metal in their cationic moiety are given poor recognition, as compared to the salts of metal in their anions. The nature of constituent metal cations with the composition of anionic specification mainly dictates the specific and other physicochemical properties of such metal-based organic salts. For example, the Lewis acidic/basic character of organic salts of metal halides could be tuned by varying the stoichiometric ratio of metal halides to organic halide salts [8]. Wu *et al.* found that imidazolium based organic salts, having chlorometallates as anions, exhibit stronger acidic nature as compared to imidazolium chloride ILs, as the metal chloride enhances electron deficiency of H atom (C-4/5) of imidazole moiety [16]. But it was observed that Ag-coordinated symmetric/asymmetric imidazolium based organic salts possess lower acidity than conventional ILs. The same group also compared two imidazolium based ILs of Tf_2N^- and BF_4^- anions with those of $ZnCl_3^-$, $HgCl_3^-$ and ReO_4^- anions, and noticed that the electrostatic interactions along with the H-bonds between the ions of metal-containing ILs were weaker. The reason behind the weakening of such interactions could be linked to the complicated conformations of conventional ILs after launching metals into them [17]. In 2020, Balischewski *et al.* synthesized a few Co, Cu and Mn containing monometallic, bimetallic and trimetallic salts of N-butylpyridinium cation and studied their melting points, conductivities and electrochemical stability windows [18]. Additionally, redox properties of metal-containing organic salts are also dependent on the composition of anionic metal complexes. In recent times, ILs have found significant importance in metal depositions or as electrolytes in fuel cells and supercapacitors [19, 20]. However, the limited solubility of metal salts in RTILs restricts their uses in electrochemical applications because of weak coordination capacity of the usual cations and anions in the ILs. The inclusion of metal ions into the respective ions of organic salts improves the solubility of metal salts in molten organic salts [17]. A thermally stable Ag containing imidazolium based IL $[Ag(EtIm)_2][Tf_2N]$ was synthesized by Schaltin *et al.* (2012) and it was utilized as an electrolyte to deposit silver metal above 65 °C [21].

Incorporation of heteropolyanions of polyoxometalates (POM) into the organic salts generates organic-inorganic hybrid materials with modified redox properties of polyoxometalates in the hybrids. Polyoxometalates are a class of compounds that possess inorganic cluster of metal-oxo complexes in their multinuclear anions. General formula of POM heteropolyanions is $X_sM_nO_m^{y-}$, where X is a central heteroatom (generally P, Si, Ge, As); M is a transition metal (e.g. V, Mo, W, Nb, Ta) present in its highest oxidation state with **m** number of oxygen atoms. The structures of these heteropolyanions are defined by their X/M ratio, where X/M ratio of 1/12 denotes Keggin structure and X/M ratio of 2/18 denotes Dawson structures of POMs. The combinations of basic Keggin and Dawson structures of POM result in the generation of further intricate structures [22]. These compounds, with great negative charge on anions due to excessive presence of oxo ligands, are greatly soluble in polar solvents which restricts their usage in various applications. Thereby, considerable modifications are done to modify POMs with organic cationic moieties, which lead to the generation of organic-inorganic hybrids of POMs. This modified class of compounds retains privileges of both the organic part (e.g. functional adaptability, hydrophilicity/hydrophobicity) and inorganic part (e.g. extended thermal as well as chemical stability). When POMs are merged into ILs by ion-exchange method, polyoxometalate hybrids of ionic liquids (IL-POMs) are formed, which is an extensively studied class of hybrid compounds in recent years. IL-POMs belongs to the 'Class I' type of hybrid polyoxometalates, where the organic and inorganic parts interact through non-covalent type of interactions like H-bonding, van der Waals attraction, electrostatic interactions etc. [23]. In the domain of catalysis, polyoxometalates are highly significant because they act as strong acids. But the acidity is observed to be enhanced by forming IL-POM hybrids with task-selective ionic liquids. Saikia and group synthesized two POM hybrids, $[mdsim]_3[PMo_{12}O_{40}]$ and $[mdsim]_3[PW_{12}O_{40}]$, of $-SO_3H$ functionalized 2-methylimidazolium cations with phosphomolybdate ($[PMo_{12}O_{40}]^{3-}$) and phosphotungstate ($[PW_{12}O_{40}]^{3-}$), respectively, to carry out nitration of aromatic compounds as catalysts. Upon determining Brønsted acidities by calculating Hammett acidity functions, it was observed that both the POM-ILs exhibit stronger acidity than the polyoxometalate precursors [24]. Kashyap *et al.* developed two IL-POMs hybrids ($[DEDSA]_3[PW_{12}O_{40}]$ and $[DEDSA]_3[PMo_{12}O_{40}]$) of N,N'-diethyldisulfoammonium cations and used them as solvent-responsive Brønsted acidic catalysts in the oxidation of alcohols [25]. It was seen that the synthesized IL-POM hybrids are thermally stable up to a high temperature as compared to their parent polyoxometalates. The physicochemical properties of hybrids of IL-POMs can also be tuned by altering the size and structure of heteropolyanions. Wu *et al.* in 2017 fabricated two thermo-responsive phosphonium-based IL-POM gels to use them as electrolytes for supercapacitors. It was observed that the hybrid having Dawson-structure, $[TBTP]_8P_2W_{16}V_2O_{62}$, was more thermally stable, low melting and highly conductive as compared to the hybrid having Keggin-structure, $[TBTP]_5PW_{10}V_2O_{40}$ [26]. A series of dicationic imidazolium polyoxotungstate hybrids are synthesized to act as phase-transfer catalysts in epoxidation of olefins in presence of H_2O_2 [27]. Thus, it was observed that the hybrid of POM-ILs offer a diverse applicability from catalysis to electrochemistry. Structures of some reported IL-POM hybrids are shown in **Fig. 1A.3**.

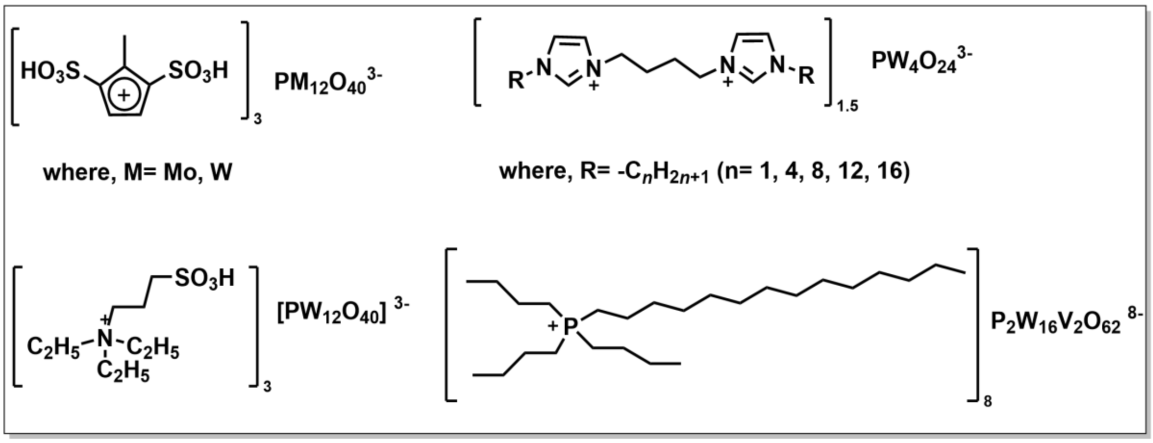


Fig. 1A.3: Structures of some reported IL-POM hybrids.

Another fascinating realm of metal-containing organic salts is halometallates, where the metal exists as complex metal halide anions (**Fig. 1A.4**). The pairing of organic cations with the complex metal halide anions forms halometallate organic salts, which are commonly fused viscous liquid or solid compounds, as governed by the molar proportion between the metal halide anion and the organic cation [8]. The composition of halometallate organic salt is described by χMX_m, which refers to the molar proportions of metal halides MX_m, i.e. when 'n' equivalents of MX_m is used to synthesize the halometallate organic salt, its χMX_m would be n/(1+n). Based on the molar ratio of metal halides, anionic speciation of halometallate organic salts is determined, which primarily controls the Lewis acidity/basicity of the organic salt. For different metals or halides, this molar proportion (χMX_m) range may fluctuate in synthesizing the halometallate ILs or organic salts from neutral ILs/organic salts, which contributes to the possible formation of more than one halometallate anions that co-exist in a dynamic equilibrium [8, 28]. However, physicochemical properties like thermal stability, moisture sensitivity, hydrophilicity/hydrophobicity, solubility, viscosity, ionic conductivity, density etc. depend on both the cations and anions of halometallates.

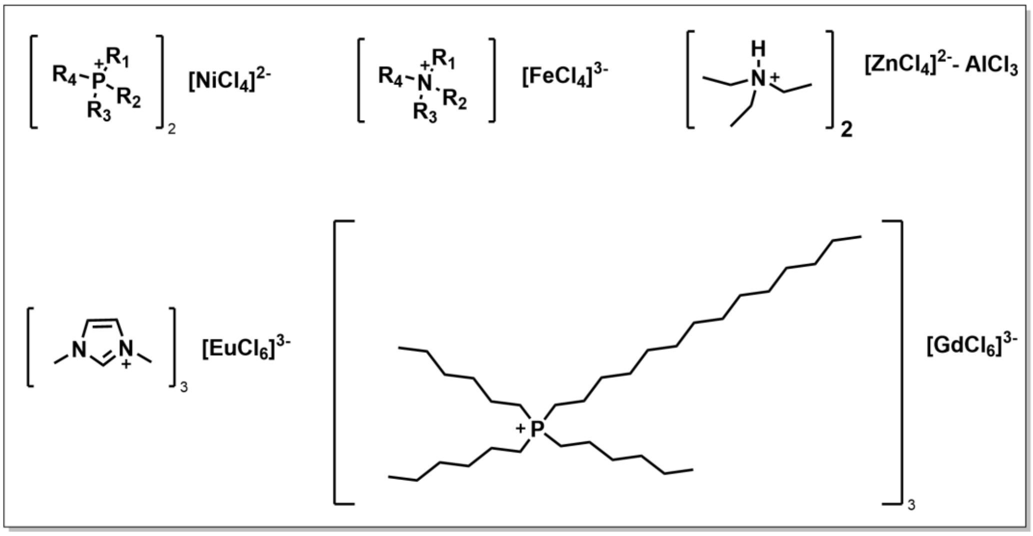


Fig. 1A.4: Structures of some Lewis acidic mono/mixed halometallate ILs.

The earliest Lewis acidic ILs studied were the chloroaluminate ILs [29, 30], mostly appeared in liquid state, but were found to be moisture sensitive for applications under atmospheric conditions. There are also some reports of chlorometallate ILs of other group IIIA metals (Ga (III) and In (III)), although less studied than Al-based ILs [31]. Nonetheless, due to the moisture sensitive nature or poor abundancy of such salts, anions of transition metals such as Zn, Fe, Sn, Ni, Co etc. were developed. These halometallate organic salts were found to be stable in air or moisture and were comparatively affordable, supporting their easy handling and uses in bulk applications [32]. Apart from the main-group metals and transition metals, halide salts of rare-earth metals are also used in the synthesis of halometallates. One such example of rare-earth metal ionic liquids (REMILs) is a series of phosphonium-cation based $[P_{666\ 14}]_3[MCl_6]$ halometallate ILs (where M= Er, Gd, Ce, Pr, Nd, Sm, Yb etc.), which exist as liquids at room temperature (all having melting points ranging from −58 °C to −40 °C). Thermal stabilities of these halometallates are found to be very high (decay temperature 340-380 °C). Some of them are found to possess photoluminescence as well as magnetic properties [33]. Furthermore, synthesis of a double salt ionic liquid (DSIL) is also reported by mixing two metal halides of non-identical Lewis acidity. When triethylammonium-based halometallate IL $[HN_{222}]_2[ZnCl_4]$ was mixed with $AlCl_3$ at different compositions, the resultant DSIL was observed to perform better catalytic activity in a Backmann rearrangement reaction than either of the parent metal halide salts. This recognizable synergistic improvement was due to the electron rich conditions, where $AlCl_3$ withdraws electron from zinc chloride anion to generate the mixed DSIL of halometallates [34]. Moreover, transition metal-based halometallates of functionalized proton-donor groups such as -SO_3H, -CH_2CH_2OH etc. in the cationic moiety are also reported [35, 36] (**Fig. 1A.5**). Such modified organic salts exhibit dual Brønsted-Lewis acidity, since the organic cations can donate protons while the complex anionic metal halides can accept electrons. These functionalized groups induce electrostatic interactions, coulomb attractions, H-bonding and/or van der Waals force among the ions, which elevate the thermal decomposition temperature of the halometallate functionalized organic salts. The increased acidity of these functionalized halometallate ILs makes them excellent catalysts or solvents in catalysis, especially in the acid-catalysed reactions.

Fig. 1A.5: Structures of some Brønsted-Lewis acidic functionalized halometallate ILs.

1A.3.1. Organic salts in the synthesis of metal nanoparticles

Although various physical and chemical processes are available to synthesize metal nanoparticles (NPs), green synthetic methods of metal NPs have gathered attractions in the recent years. Organic salts, especially the room temperature ILs, are also broadly studied as solvent in the synthesis of nanoparticles after it was noticed that they effectively stabilize metal-NPs [37]. The most commonly used ILs having 1,3-dialkylimidazolium cations and weakly co-ordinated $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$ etc. anions, with required thermal and electrochemical stability, serve as efficient reaction media as they maintain the liquid state over a wide range of temperature. Apart from it, they can be also used as catalysts, stabilizers and templating factors in the metal-NP synthesis. For preparation of the metal nanoparticles, the metal salts are reduced by external reductants like NH_2NH_2, $NaBH_4$ and H_2, or internal reductants which are present within the ILs such as protic anions (acetate, acetylacetonate etc.) or cations having proton at C-2 position of the imidazolium ring.

The constituent ions of ionic liquid medium help to stabilize the metal-NPs by prohibiting their agglomeration. The process of limiting the agglomeration of metal NPs is done by causing repulsion between the NPs in an electrostatic manner, steric manner or sometimes both. In the electrostatic stabilization, the repulsive Coulomb forces are intensified, while the attractive van der Waals interactions are diminished with the help of electrical double layer (Debye layer), which is generally formed between the NPs and the ionic components of an IL [38]. Criteria such as temperature, pH, thickness of the Debye layer etc. also influence the efficacy of electrostatic stabilization [39]. Steric stabilization comes from capping ligands such as alcohols, thiols, carboxylates, polymers, surfactants etc., as these ligands facilitate the steric repulsion between the NPs [40]. In presence of ILs, fusion of both electrostatic as well as steric stabilization (electrosteric) is observed in the metal-NP synthesis. ILs with alkyl side chain exhibit dual electrostatic-steric stabilization effect as various N-heterocyclic cationic ILs form electrical double layer around the metal-NPs, forcing the nanoparticles to avoid each other. With the alteration of cations/anions in different ILs, physicochemical parameters like viscosity, thermal stability, conductivity, density etc. are also transformed, which is likely to influence the growth and morphologies of metal NPs. One such example is the synthesis of Cr, Mo and W metal NPs from precursor metal carbonyls in imidazolium-based ILs with anions of different sizes, where the anion with bigger volume $[(CF_3SO_2)_2N]^-$ yielded larger-sized nanoparticles as compared to relatively smaller $[CF_3SO_3]^-$ and $[BF_4]^-$ anions [41].

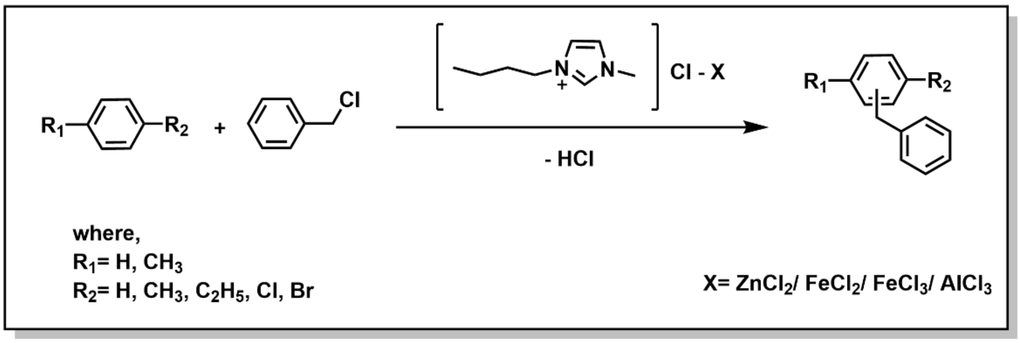
Again, it was noticed that ILs having $[BF_4]^-$, $[PF_6]^-$, $[NTf_2]^-$ anions, that offer weak co-ordination ability to the 1,3-dialkylimidazolium counter-cations, are considered to be preferable stabilizers than ILs with $[N(CN)_2]^-$ anion. Additionally, it was also observed that metal-NPs of Au or Cu were stable for a longer period without agglomeration in 1,3-dialkylimidazolium cations of comparatively shorter alkyl chain length (e.g. butyl) than in those with longer alkyl chain length (e.g. octyl or trihexyltetradecyl). Thus, it is safe to mention that ILs with short alkyl chain bearing cations and weakly associative $[BF_4]^-$, $[PF_6]^-$, $[NTf_2]^-$ etc. anions act as qualitatively better stabilizer than ILs with longer alkyl chain bearing cations and strongly coordinating $[N(CN)_2]^-$ anion [42]. Besides the roles of cations and anions, the influence of functionalized ILs on the formation of metal nanoparticles is also unavoidable. It was found that rapid formation of smaller sized Pd NPs from $Pd(OAc)_2$ occurred in a series of ILs with hydroxyl group-functionalized cations, as compared to the NPs formed in non-functionalized IL. Oxidation of the formed nanoparticles was also hindered by the functionalized ILs [43]. Another set of novel functionalized imidazolium ILs, with thiol groups attached to different positions of cations or anions, were developed as stabilizing agents to synthesize small sized Au or Pt NPs. The total number along with the positions of thiol groups in the ILs control even distribution and size of the formed nanoparticles [44].

Furthermore, ILs with cations having C-H bond such as imidazolium can form hydrogen-bonds with anions containing electronegative atoms like F or O, which provides structural directivity to the nanoparticles formed. Again, H-bonds can also be formed between the ions in ILs and metal complexes with hydroxide, oxido etc. ligands. In such cases, competition between the extent of various internal and external H-bonds determine the stability of metal-NPs in ILs [45]. However, ILs that do not have acidic C-2 proton in the cation are found to perform as average stabilizers, as rapid growth as well as aggregation of metal-NPs are observed, which affect the morphology and size of the nanoparticles [42]. Other than the transition metal NPs, synthesis of stable lanthanide fluoride NPs of Y^{3+}, Eu^{3+} and Tb^{3+} are also reported in 1-butyl-2-methylimidazolium tetrafluoroborate IL, where the IL acts as the source for fluoride anion [46]. Overall, the syntheses of metal NPs are done by several processes like heating, stirring/grinding at room temperature, electrochemical methods, ultrasound irradiation, microwave irradiation etc. [47]. Such metal NPs, developed in ILs, are being extensively used in the field of homogeneous/heterogeneous catalysis, photocatalysis, luminescence, sensing/biosensing, separations, fuel cell catalytic processes etc., as the desired size and morphology of the NPs can be designed accordingly [48].

1A.4. Importance of halometallate organic salts in catalysis

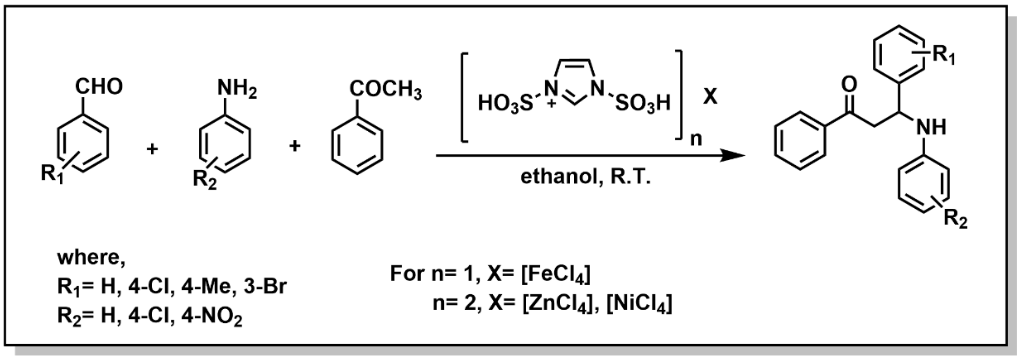
Halometallate organic salts are fundamentally distinguished as Lewis acidic ILs, by virtue of the complex metal halide anions present in them. Based on the ratio of metal halide to organic salt, more than one anionic species can exist in equilibrium in a halometallate organic salt. For example, treatment of equimolar amount of anhydrous $AlCl_3$ with organic chloride, such as ammonium/imidazolium/pyridinium chloride, could produce chlorometallate of organic cation with composition [cation][$AlCl_4$]. Further addition of $AlCl_3$ to the [cation][$AlCl_4$] may lead to formation of [cation][Al_2Cl_7] and [cation][Al_3Cl_{10}] salts. It was found that depending on the mole fractions of $AlCl_3$ ($\chi AlCl_3$) used, the chloroaluminates would be neutral, Lewis acidic or Lewis bases in nature. At $\chi AlCl_3 = 0.5$, the organic salt becomes neutral, where the only anion is AlC_4^-. Lewis basic chloroaluminate is observed at $\chi AlCl_3 < 0.5$ (i.e. high amount of organic chloride salt). However, at $\chi AlCl_3 > 0.5$, Lewis acidic chloroaluminate is formed, where multinuclear anions of aluminium chloride exist together in equilibrium [49]. It was also seen that Lewis acidity of the metal halide containing organic salts is often found to be greater than precursor metallic halides. Such examples include the synthesis of 1-allyl-3-methylimidazolium [amim]$^+$ salts with $CoCl_3$, $FeCl_4$, $ZnCl_3$, $MnCl_3$ and $CuCl_3$ anions by mixing anhydrous metal chloride salts with 1-allyl-3-methylimidazolium chloride [amim]Cl. Their Lewis acidic catalytic activities were screened for glycolytic conversion of poly(ethylene terephthalate) (PET) to bis(hydroxyethyl) terephthalate (BHET) under mild conditions in ethylene glycol. Among them, excellent %conversion of PET (up to 100%) and %selectivity (~80%) to BHET were observed in case of [amim]$ZnCl_3$ and [amim][$CoCl_3$]. These degradation results were also found to be better than the use of $ZnCl_2$ or conventional IL catalyst. Another advantage was the easy separation of highly pure BHET products from the halometallate catalysts. This enhanced catalytic activity was credited to synergistic action of [$ZnCl_3$]$^-$ anion and [amim]$^+$ cation, where [$ZnCl_3$]$^-$ associated with the -OH hydrogen of ethylene glycol and the electron-deficient [amim]$^+$ cation interacted with the ester group oxygen in PET, leading to breakage of long chain in PET [50]. Further modification of the same glycolytic degradation reaction of PET to yield

BHET in ethylene glycol was done by Shuangjun and co-workers [51]. In this modified reaction, mixed Lewis acidic halometallate ILs were developed as PET degradation catalysts by mixing metal chlorides of Zn(II), Co(II), Fe(III), Cu(II) with 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl) at various molar ratios. At 1: 0.5: 0.5 molar ratio of [Hmim]Cl: $ZnCl_2$: $CoCl_2$, 87.1% yield of the BHET product was observed, which was significantly higher than BHET yield% of any individual halometallate used by Wang *et al.* [50]. Thus, it is evident that incorporation of metal halides into the conventional ILs or organic salts does enhance the Lewis acidic property of the ILs/organic salts [51]. In addition, other catalytic reactions like alcoholysis of polycarbonates [52], hydrochlorination of acetylene [53], hydrosilylation of olefins [54], Friedel-Crafts benzylation to synthesize diphenylmethane and derivatives (**Scheme 1A.1**) [55], Knoevenagel condensation to prepare electrophilic alkenes [56], deep oxidative desulfurization of fuels [57] etc. were carried out in presence of various Lewis acidic halometallate organic salts/ILs.

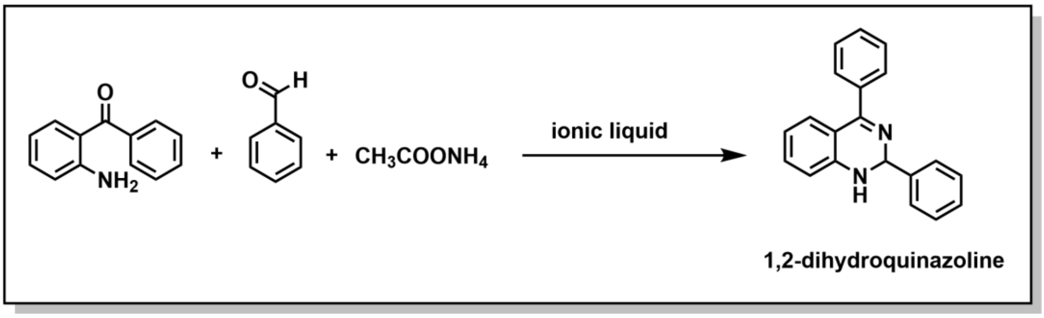


Scheme 1A.1: Lewis acidic halometallate ILs catalysed Friedel-Crafts benzylation reaction [55].

Attachment of H-donor functional groups like -COOH, $-SO_3H$ etc. in the organic cations of Lewis acidic halometallates would provide Brønsted acidity in these salts and thus leads to formation of Brønsted-Lewis acidic halometallate organic salts. The presence of both proton donor and electron acceptor groups in such dual Brønsted-Lewis acidic halometallate ILs substantially boost their acidic nature. A series of 1,3-disulfoimidazolium salts of $[ZnCl_4]^{2-}$, $[FeCl_4]^{-}$ and $[NiCl_4]^{2-}$ anions were prepared as catalysts to synthesize β-amino carbonyl compounds at room temperature (**Scheme 1A.2**) [58]. They highlighted the contribution of both the Brønsted acidic $-SO_3H$ group and the Lewis acidic chlorometallate anions in the improved outcomes of the reaction. The same group also carried out the efficient synthesis of *bis*-(indolyl)methanes by another set of Brønsted-Lewis acidic chlorometallate organic salts as catalysts [59]. They also developed phosphonium cation based Brønsted-Lewis acidic chlorolometallates of transition metals as effective heterogenous catalysts to synthesize 2,3-dihydro-1,2,3-trisubstituted-1*H*-naphth[1,2-e][1,3]oxazines in a multi-component reaction [35]. Likewise, more Brønsted-Lewis acidic halometallate organic salts/ILs are utilized in other catalytic reactions such as the conversion of chitosan to 5-hydroxymethylfurfural in water medium [60], conversion of cellulose into 5-hydroxymethylfurfural [61], cellulose conversion to levulinic acid [62], alkylation of isobutane/isobutene [63], oxidative desulfurization of fuels [64] etc. By observing the catalytic efficiencies of Brønsted-Lewis acidic halometallates in acid catalysed organic reactions, one objective was kept for designing of sulfonic acid functionalized piperazinium cation-based halometallate salts of transition metal chlorides as catalysts in the multicomponent synthesis of quinazoline derivatives (**Scheme 1A.3**).



Scheme 1A.2: Brønsted-Lewis acidic halometallate ILs catalysed synthesis of β-amino carbonyls [58].



Scheme 1A.3: Multicomponent synthesis of quinazolines derivatives (1,2-dihydroquinazolines) using acidic ionic liquids.

1A.4.1. Literature review on the synthesis of quinazoline derivatives

Quinazolines are a broad category of N-heterocyclic compounds that offer medicinal importance owing to their biologically active pharmacophore. They have gained considerable recognition owing to their varied pharmacological activities like anticancer, antibacterial, antimalarial, anti-inflammatory, antifungal, antimicrobial, antihypertensive etc. [65-67]. Quinazolines and their derivatives also effectively participate in some biological events such as blocking cellular phosphorylation [68], DNA binding [69], blocking T-type calcium channel [70] etc. They also act as the building blocks for several alkaloids that exist naturally in some microorganisms, plants and animals [71]. Such therapeutic relevance and diverse implementation of quinazolines and their derivatives appeal for the need of their effortless synthesis.

Kumar *et al.* carried out rapid synthesis of substituted quinazolines and quinazoline derivatives in domestic microwave-assisted reactions, with satisfactory product yields under solvent-free and catalyst-free conditions [72]. Another microwave-promoted reaction, that is fast, recyclable and high-yielding under a mild-reaction condition, is the synthesis of dihydroquinazolines from 2-(aminoaryl)alkanone *O*-phenyl oximes and substituted aldehydes in toluene. Also, the addition of Lewis acidic $ZnCl_2$ to this system led to the formation of quinazolines [73]. 1,2-dihydroquinazolines and quinazolines are also synthesized by microwave-irradiated one-pot reaction of 2-aminobenzophenone, aldehydes and urea at 540 W and 130 °C in 4 min of reaction span in absence of solvent or catalyst [74]. Photochemical irradiation of oxime derivatives in acetonitrile with a 400 W mercury light source produced up to 98% of quinazoline product in 1-3 h of reaction [75]. Transition metals such as Pd [76], Cu [77] etc. based catalysts were also reported to be employed in quinazoline derivative synthesis. A silica-supported Fe_2O_3 nanocomposite was developed as a heterogenous recyclable catalyst in ethanol mediated one-pot three-component reaction for quinazoline derivative synthesis under mild conditions [78]. Another catalyst-free synthesis of quinazoline derivatives was done in presence of sodium hypochlorite as oxidant in a one-pot two-step cross-hydrogenative coupling reaction of 2-aminobenzylamines with aldehydes. With this method, moderate to high product yields were obtained at room temperature by using a cheaper oxidant without needing to isolate the reaction intermediate [79]. While 4-(N,N-dimethylamino) pyridine (DMAP) in ethanol produced good yields of quinazoline derivative products [80], ethanol-mediated catalyst-free synthesis was also reported at 60 °C temperature [81]. One pot synthesis of 1,2-

dihydroquinazolines from the reaction of 2-aminobenzophenone, substituted aldehydes and ammonium acetate was done with 30 mol% sulfamic acid catalyst in ethanol at 60 °C temperature. This 'green' catalyst was also recyclable, which generated great amounts of products within an hour of reaction span [82]. The benign synthetic method of quinazoline derivatives was established in acetic acid medium under reflux conditions to produce high product yields within a short reaction time [83].

Some reports also revealed the use of ILs in quinazoline synthesis. The Brønsted acidic IL 1-methylimidazolium triflouroacetate ([Hmim]TFA) was employed as a catalyst in the multi-component synthesis of quinazoline derivatives under solvent-free conditions at 80 °C temperature. Together with aerobic oxidation, [Hmim]TFA effectively produced excellent product yields by avoiding the use of organic solvents, where catalyst recyclability was possible for up to three times with negligible loss in catalytic activity [84]. Fatehi *et al.* developed a magnetic nanomaterial of piperidinium based silica-coated Fe_3O_4 (piperidinium benzene-1,3-disulfonate salt (PBDS-SCMNPs)) along with another ammonium-based salt (triethanolammonium-2,2,2-trichloroacetate (TEATCA)) for quinazoline derivative synthesis in ethanol-water under reflux condition. It was found that PBDS-SCMNPs exhibit several advantages as compared to TEATCA in the productivity of the reaction [85]. The use of Lewis acidic IL [bmim][$FeCl_4$] generated an eco-friendly and atom-efficient multi-component synthesis of quinazolines under-solvent free conditions at 40 °C temperature. This magnetic catalyst was effectively recyclable and high yielding with a short reaction time [86]. **Fig. 1A.6** shows structures of some reported catalysts that are used in the synthesis of quinazolines and quinazoline derivatives.

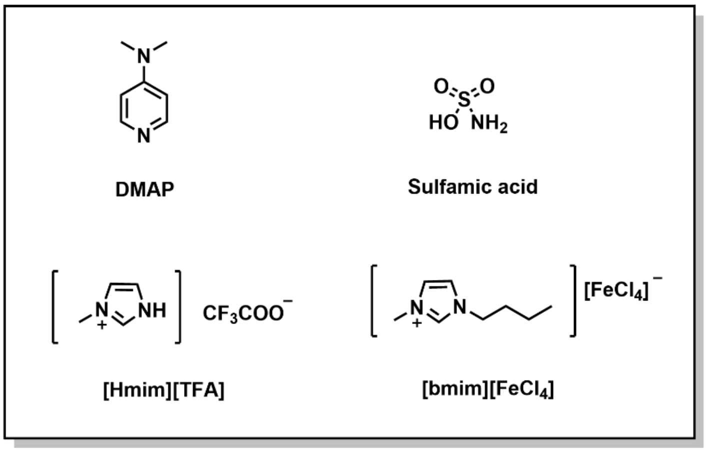


Fig. 1A.6: Structures of some reported catalysts that are used in the synthesis of quinazolines.

1A.5. Organic-inorganic hybrid salts of permanganate and their significance

Potassium permanganate is known as a multifaceted traditional oxidant, which is meticulously used in synthetic organic/inorganic chemistry for years. This commercially available oxidant offers eco-friendly oxidation processes and hence gained immense utility for oxidation of various organic substrates like alcohols, aldehydes, olefins, sulfides, saturated C-H bonds and compounds containing other functional groups [87]. However, $KMnO_4$ exhibits poor selectivity in oxidation reactions and often causes the formation of over-oxidized products. Other disadvantages include poor solubility of most organic substrates in aqueous solution of $KMnO_4$ and thermodynamical instability of $KMnO_4$ in water [88]. Some of these problems were modified by associating MnO_4^- anion with organic cations like ammonium/phosphonium, with varying alkyl side chains without any functional groups attached to them, to develop organic-inorganic hybrid salts. Examples of such types of organic-inorganic hybrids of permanganate anion include tetrabutylammonium permanganate (TBAP) [89], cetyltrimethylammonium permanganate (CTAP) [90], benzyltriethylammonium permanganate (BTAP) [91], methyltributylammonium permanganate (MTBAP) [92] etc. Most of them are prepared by continuously stirring aqueous solution of tetraalkylammonium halide with aqueous $KMnO_4$ solution (1:1 equivalent of both reagents) at room temperature. The resultant hybrid materials are mostly soluble in dichloromethane, chloroform, acetone, glacial acetic acid and some are sparingly soluble in water. They exhibited commendable performances in oxidation as well as dihydroxylation reactions, by enhancing unique characteristics while lowering the drawbacks of individual units [88]. The use of CTAP was observed as potent oxidant for hydroxylation of alkenes by different methods to get *cis*-dihydroxylated products [90, 93]. It also oxidized an active drug ingredient carbamezpine (CBZ) in dichloromethane solvent to form a cyclic ester intermediate, which underwent decomposition followed by hydrolysis to form dicarbonyl product [94]. It was also used for oxidative regeneration of carbonyl compounds from several aldoximes or ketoximes by grinding at room temperature [90, 95]. Nevertheless, some ammonium and phosphonium based organic-inorganic hybrids display low decomposition temperatures [96]. The hybrid BTAP was found to explode after a particular induction period depending on temperature [91]. In addition, some of them also undergo self-oxidation in certain organic solvents [88]. To overcome the limitations of various known organic cation-based permanganate hybrids as oxidants, it was planned to develop thermally stable N-sulfonic acid functionalized ammonium and imidazolium-based permanganate hybrids for potential uses as recyclable oxidative catalysts for conversion of alcohols to keto compounds and selective oxidation of organic sulfides to sulfoxides in aqueous solutions under mild conditions.

1A.5.1. Literature on oxidation of alcohols by permanganate-based organic-inorganic hybrid salts

Selective oxidation of primary/secondary alcohols to aldehydes/ketones is considered as an essential transformation as it possesses chemical and biological relevance [97]. Aldehydes and their derivatives are known to possess various antibacterial [98], antimicrobiobial [99], antioxidant and immunomodulatory properties [100]. Some aldehyde derivatives may be responsible for natural fragrances like essential oils that are used in aromatherapy, while some are extensively utilized in cosmetics industry, food industry etc. [100]. Some commercially available aldehydes are also noticed to be utilized in drug designing [101]. Hence, easy and effective synthesis of aldehydes/ketones by oxidizing primary/ secondary alcohols holds major importance. For this, the role of oxidant is crucial as it requires to effectively carry out the conversion under mild conditions without forming undesired side-products, while being eco-friendly and non-hazardous to use at the same time.

Among different types of traditional strong non-selective transition metal-based oxidants [102, 103], potassium permanganate ($KMnO_4$) is a powerful oxidant that oxidize primary alcohols to aldehydes or acids, and secondary alcohols to ketones in acidic, basic or neutral media [104, 105]. However, in most cases, $KMnO_4$ is used as aqueous solution which limits its implications as oxidants due to the insoluble nature of most organic compounds in water medium [106]. In addition to that, the oxidizing power of $KMnO_4$ is reduced due to slow decomposition in water to MnO_2, O_2 and OH^- ions, which is further accelerated in presence of MnO_2 as well as under acidic and basic conditions [104]. Such degradation of $KMnO_4$ enforced its usage in non-stoichiometric amount, which often led to the formation of over-oxidized products, lowering the yields of desired oxidative products and violated 'atom economy concept' of sustainable chemistry by generating significant amounts of waste materials to the environment. Later, the solubility issue of organic substrates in aqueous $KMnO_4$ was dealt with by introducing phase transfer catalysts. Although the solubility of organic substrates improved in aqueous $KMnO_4$ in presence of phase transfer catalysts, over-oxidized acidic products were obtained in the oxidation of primary alcohols [107]. For example, Jose *et al.* added 18-crown-6, as phase-transfer catalyst, to a solution of $KMnO_4$ in benzene. After stirring the solution until the appearance of clear purple colour, benzyl alcohol was added to the solution, which resulted in the formation benzaldehyde as the sole product. But with the increase in temperature and catalyst amount, selectively of the reaction system was affected and formation of benzoic acid was also observed along with benzaldehyde [106]. Therefore, reactivity of $KMnO_4$ had to be re-modified by supporting $KMnO_4$ on some solid materials. Shaabani *et al*. carried out selective oxidation of primary and secondary alcohols to aldehydes and ketones by supporting $KMnO_4$ on copper sulfate pentahydrate ($CuSO_4.5H_2O$) or alumina (Al_2O_3) or a mixture of both (Al_2O_3-$CuSO_4.5H_2O$) under solvent-free conditions [108]. To prepare the oxidizing system, $KMnO_4$ and $CuSO_4.5H_2O$ were taken in a mortar in equal amounts and then grinded until complete homogeneous mixture was obtained. Alternatively, the mixture of equal amount of $CuSO_4.5H_2O$ with a paste of alumina in concentrated aqueous $KMnO_4$ solution was grinded to get another oxidizing system. The reaction was conducted at room temperature by taking 2 mmol of substrate in 4 g of prepared $KMnO_4$/solid support as oxidant, which led to the formation of aldehyde/ketone products with high yields during 4-6 h reaction. They also developed more systems like $KMnO_4/MnO_2$ [109] and $KMnO_4$/montmorillonite K10 [110] for the same purpose. Firouzabadi *et al.* used 20-30 mmol $KMnO_4/ZrOCl_2.8H_2O$ oxidant system to oxidize 10 mmol of alcohol [111]. Lou and group developed a few $KMnO_4$/solid support systems such as $KMnO_4$/Graphite [112], $KMnO_4$/silica gel [113], $KMnO_4$/aluminium silicate [114], $KMnO_4$/kieselguhr reagent [115] etc. as oxidants in heterogeneous synthesis of carbonyl compounds from alcohols under solvent-free condition or in aqueous/toluene medium. Such modified oxidant/solid support systems considerably increased the product selectivity of $KMnO_4$, but most of these methods used excess amounts of $KMnO_4$/solid support reagents, as compared to the substrate alcohols.

Further, some oxidation methods engaged ILs as reaction medium with $KMnO_4$ as oxidant, as ILs are widely used as greener solvents. Kumar *et al.* reported a mild approach to selectively oxidize benzylic alcohols to produce corresponding carbonyl compounds with $KMnO_4$ in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] as solvent [116]. The oxidation was carried out at room temperature and 83-97% of carbonyl products were obtained in 2 h. The IL was also recycled up to fifth cycle. Another IL 1-butyl-3-methylimidazolium bromide [bmim][Br] mixed acetonitrile solvent selectively generated carbonyl products from several benzylic and aliphatic alcohols at room temperature [117]. In this method, lesser amount of $KMnO_4$ was required to produce highly pure products with more than 80% yield in short reaction period. Another combined triazine-based recyclable oxidative IL system [TAIm][MnO_4]/[TAIm][OH], containing 1,1’,10”-(1,3,5-triazine-2,4,6-triyl)tris(3-methyl-1*H*-imidazol-3-ium) ($[TAIm]^+$) as organic cation, was developed by Jasim and co-workers [118]. They employed this system for gram scale homogeneous aerobic oxidation of alcohols, where the substrate was stirred with [TAIm][I], [TAIm][OH] and $KMnO_4$ in deionized water at room temperature to selectively generate excellent carbonyl product yield within 4 h. One notable aspect of this method was the transfer of $KMnO_4$ salt to a safe and stable [TAIm][MnO_4] ionic liquid. Some other reports of using organic-inorganic hybrid salts of permanganate in oxidation of alcohols are also available. Cetyltrimethylammonium permanganate (CTAP) was developed as a stable organic-inorganic hybrid by stirring cetyltrimethylammonium bromide (CTAB) with $KMnO_4$ in water at room temperature. It selectively oxidized various benzylic alcohols to aldehydes without causing over-oxidation of the products but converted the aldehydes into carboxylic acids when treated separately [119]. Das *et al.* also used CTAP in the oxidation of benzyl alcohols to aldehydes in chloroform, although self-oxidation of CTAP might occur in this method [120]. Another similar organic-inorganic hybrid tetrabutylammonium permanganate (TBAP) was prepared by stirring tetrabutylammonium bromide (TBAB) with aqueous $KMnO_4$ at room temperature. It was used as an oxidant for conversion of various organic substrates, such as aromatic aldehyde, benzyl alcohol, *p*-nitrotoluene and *cis*-stilbene, to acid products at room temperature in pyridine [89]. Nore *et al.* used benzyl(triethyl)ammonium permanganate (BTAP) in the oxidation step during the synthesis of furocoumarins such as methoxalen, which is used in certain medicines for skin diseases [121]. Structures of some permanganate-based organic-inorganic hybrids that were used in alcohol oxidations are given in **Fig. 1A.7**.

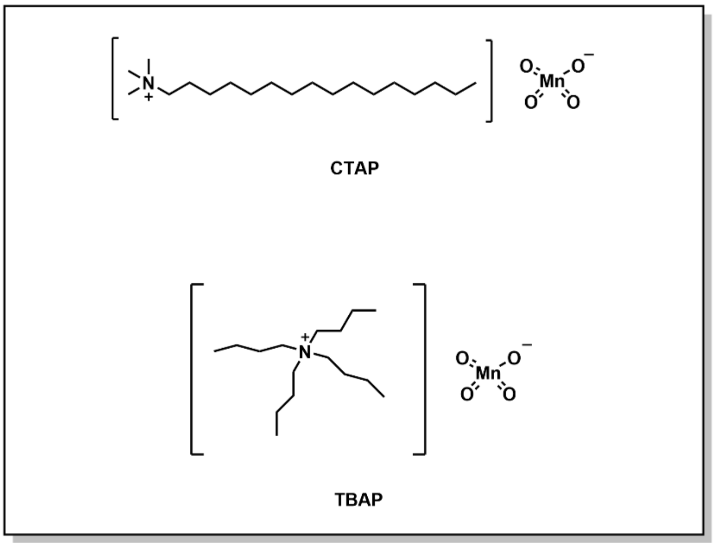


Fig. 1A.7: Structures of some permanganate-based organic-inorganic hybrids that were used in alcohol oxidation reactions.

1A.5.2. Significance of organic sulfide oxidations and literature on oxidation of organic sulfides involving permanganate-based oxidants

Oxidation of organic sulfides is one of the important conversion reactions in chemical industry, since the products sulfoxides and sulfones have a wide range of applications in chemical, biological and pharmaceutical fields [122-126]. Sulfoxides act as beneficial synthons in Diels-Elder reactions [127], C-C bond forming reactions [128] etc. Most chiral sulfoxides or sulfones are widely used as auxiliaries in asymmetric synthesis that possess high biological activity [128-130] or as ligands in the formation of metal complexes [131]. Likewise, allylic sulfoxides [132] and cyclic sulfoxides/sulfones are used as reaction intermediates for preparation of drug molecules [133]. Some of these oxidized products of organic sulfides are also employed for synthesis of lubricants, crop protecting agents in agriculture and veterinary drugs [134]. Enantiopure sulfoxides like omeprazole, pantoprazole, rabeprazole etc. act as proton pump inhibitors to treat stomach ulcers and acid reflux [135], while some other sulfoxides take part in enzyme activation [136]. Furthermore, dimethyl sulfoxide (DMSO) is extensively utilized as reaction medium, and analytical solvent as well as multipurpose reactant [137, 138]. In addition, hydrodesulfurization (HDS) process that effectively removes sulfur contents like thiols, sulfides and disulfides from fuel demands harsh conditions to remove sterically hindered organic sulfides like 4,6-dimethyldibenzothiophene (4,6-DMDBT) [139]. However, when oxidative desulfurization process is used instead of HDS, DBT or its derivatives are removed by oxidizing them to their sulfoxide/sulfone forms under mild conditions [140].

Although numerous ways for oxidization of sulfides to sulfoxides are reported, most of these processes used multiple reagents in non-stoichiometric amounts that lead to the formation of over-oxidized products, making them less appealing for large-scale syntheses [141-143]. But the diverse applicability of this oxidative conversion calls for easy and effective methods involving catalysts, oxidants and solvents that are eco-friendly and generate less wastes. As per some reported methods, the 'greener' oxidant hydrogen peroxide (H_2O_2) selectively oxidized organic sulfides to sulfoxides in imidazolium/pyridinium-based ILs under mild conditions [140, 144, 145]. Many supported/non-supported polyoxometalates are either immobilized in ILs to develop polyoxometalate complexes in ILs or inserted in ILs to develop polyoxometalate salts of ILs to conduct sulfide oxidation with H_2O_2 as oxidant under mild conditions [146-150]. Among the varied types of metal-based oxidants [151-154], comparatively cheaper traditional catalyst $KMnO_4$ was also used from a long time to conduct the oxidation process of sulfides. Bordwell *et al.* reported the use of $KMnO_4$ in basic aqueous solution under reflux temperature, where excess amount of $KMnO_4$ generated poor to moderate yields of sulfones [155]. Later, sulfoxides were obtained from organic sulfides with $KMnO_4$ oxidant via a single-step electrophilic shift of oxygen atom from permanganate anion, where the kinetics of the oxidation reaction were also studied [156]. Lee and coworkers investigated a mechanistic study of oxidation of (phenylthio)acetic acid to (phenylsulfonyl)acetic acid in basic solution with excess amount of $KMnO_4$ to get moderate yields of products [157]. Shaabani *et al.* reported a solvent-dependent oxidation method, where $KMnO_4$ converted the sulfides to sulfoxides in CH_3CN medium and to disulfides in CH_2Cl_2 medium [158]. Theoretical calculation, done by Arumugam *et al.*, revealed a mechanism where sulfide oxidation was carried out via 1,3-dipolar cycloaddition of permanganate [159]. The non-selective nature of $KMnO_4$ along with poor yield of product was tried to improve by supporting $KMnO_4$ on solid compounds. The system $KMnO_4/MnSO_4.H_2O$ was developed by grinding $KMnO_4$ and $MnSO_4.H_2O$ together in 1:1 and 5:1 ratio [160]. The resultant solid support oxidant was added to the sulfide reductant in solvent-free as well as CH_2Cl_2 medium under heterogeneous conditions, where excellent %yield of sulfoxide products was obtained in solvent-free medium in a comparatively shorter reaction period than the homogeneous medium. Similarly, other solid support oxidative systems such as $KMnO_4$/alumina [161],

$KMnO_4/MnO_2$ [162], $KMnO_4$/montmorillonite K10 [163] etc. were also developed for the same purpose. However, most of these methods used excess amount of $KMnO_4$/solid support reagents pointing towards their lower reactivity, while some methods still lacked product selectivity. Organic-inorganic hybrid salts of permanganate oxidant were also employed in oxidation of sulfides [88]. Benzyltriethylammonium permanganate (BTAP) oxidized various linear sulfides to sulfone products in CH_2Cl_2/CH_3COOH medium at -10 °C [164]. Other organic-inorganic hybrids such as methyltriphenylphosphonium permanganate [165] and tetra-*n*-butylammonium permanganate [166] etc. were also employed in oxidation reactions. However, these ammonium permanganates were unstable above ambient temperature and possess explosive nature, which required careful handling of freshly prepared reagents and thereby, had limited applicabilities. However, a thermally stable (up to 110 °C) oxidant *N, N'*-dibenzyl-*N,N,N',N'*-tetramethyl diammonium permanganate (DBTMEP) (**Fig. 1A.8**) was developed by Lakouraj *et al.* that selectively converted sulfides to sulfones within 2 min at room temperature but decomposed violently on rough grinding [167].

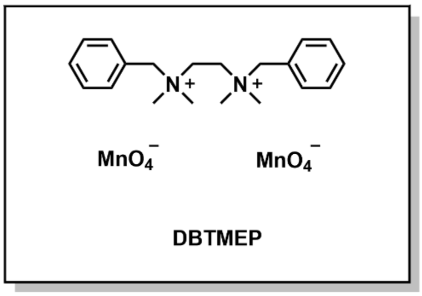


Fig. 1A.8: Structure of *N,N'*-dibenzyl-*N,N,N',N'*-tetramethyl diammonium permanganate (DBTMEP).

1A.6. Significance of organic pollutant degradation and Literature on Ag based ZnO nanocomposites as photocatalysts

Organic dyes have been extensively used in various industries such as textiles, food, cosmetics, medicine, paint etc. for ages [168-171]. Although natural dyes are comparatively less toxic, less allergic and biodegradable, synthetic organic dyes are mostly non-biodegradable and can also be carcinogenic under certain circumstances [172]. For example, benzidine (an aromatic amine) is widely used as an ingredient to develop hair dyes, which is known to be a potential carcinogen to cause urinary bladder cancer [173]. Moreover, the exposure of such synthetic dyes to nature in large amounts can cause serious environmental issues like difficulty in waste management, contamination of water/soil etc. [171, 174]. Hence, degradation of the organic pollutants/dyes to ecologically harmless compounds hold immense significance. Many of the conventional routes for dye degradation are found to exhibit several drawbacks like involvement of costly reagents/auxiliaries, secondary pollution such as large amounts of sludge generation, deterioration in water quality, restricted application etc. [175, 176]. To overcome such problems, advanced oxidation processes (AOP) were developed as alternative techniques which include the usage of H_2O_2, O_3 or Fenton's reagents etc. [177]. Later, some modified AOPs employed semiconductors in the photocatalytic degradation of dyes or other organic pollutants [177, 178]. Semiconductors like ZnO or TiO_2, that exhibited comparatively wide band gaps, were good choices in this purpose [177, 179]. The semiconductor ZnO has a band gap of 3.3 eV and has found extensive attention as a photocatalyst due to low cost, ecofriendly character and high thermal/electrochemical stability [180, 176]. In addition, the morphology of ZnO can easily be altered by changing concentrations of precursor reagents, pH, temperature, synthetic methods etc. [179]. However, the inefficient separation of electron/hole pairs in ZnO causes their rapid recombination, which affects the photocatalytic behaviour of ZnO [181]. Additionally, other disadvantages like corrosion, deactivation, agglomeration, difficulty in reuse etc. are also related to ZnO as semiconductor [181, 182]. To overcome such drawbacks, noble metals such Ag, Au or Pt in small quantities are introduced to ZnO to develop the nano-heterostructure composites, where the charge carriers are separated to prevent their rapid recombination [183-185]. Considering the low cost and easy availability of Ag as compared to Au or Pt, numerous studies on the synthetic routes and photocatalytic behaviour of Ag containing ZnO nanocomposites have been reported. Liang *et al.* synthesized 3D flower-shaped Ag/ZnO nanocomposites by first preparing ZnO by using a simple precipitation method at 60 °C temperature, after which the Ag metal was deposited on the surface of ZnO by photoreduction process [186]. It was observed that the presence of Ag metal did not alter the 3D flower shape of ZnO in the nanocomposite. The nanocomposite resulted in enhanced photocatalytic activity than pure ZnO in the degradation of Rhodamine B dye, in the presence of UV light as well as visible light. Zheng *et al.* developed Ag/ZnO heterostructure nanocrystals *via* a solvothermal method using ethanol as solvent at 160 °C in 24 h for photodegradation of methyl orange (MO) under UV light [187]. Subhan and co-workers fabricated Ag/ZnO nanocomposites by co-precipitation method to use it as photocatalyst in the degradation of methyl violet 6B in presence of UV light or visible light [188]. Other methods like microwave-assisted or ultrasound-assisted synthesis of Ag/ZnO nanocomposites were also reported for the UV light irradiated or visible light irradiated degradation of methylene blue dye [189, 190]. In addition, protein-assisted synthesis of ternary Ag/Ag_2O/ZnO nanocomposites was reported by Ding *et al. via* hydrothermal method, where the resultant catalyst was able to photodegrade methylene blue under simulated visible light [176]. In this case, the protein bovine serum albumin acted as a complexing agent and the photocatalytic efficiency of Ag/Ag_2O/ZnO was found to be greater than ZnO, Ag_2O or Ag/ZnO. Similarly, one-step calcination method was employed in the synthesis of Ag/Ag_2O/ZnO nanocomposites to use it in the decomposition of organic pollutant dibutyl phthalate [182]. Here, the loading of Ag and Ag_2O on ZnO increased the pore volume, which consequently improved the active sites on the photocatalyst. Again, graphene oxide supported Ag/Ag_2O/ZnO nanostructures were also developed *via* formation of an amide bond between 3-aminopropyl triethoxysilane functionalized Ag/Ag_2O/ZnO and carboxylated graphene oxide [175]. The graphene oxide anchored Ag/Ag_2O/ZnO photocatalysts (Ag/Ag_2O/ZnO/GO) were used to degrade acid blue 74 under visible light irradiation. Moreover, IL-assisted syntheses of Ag containing ZnO nanocomposites were also reported in literature. As discussed in the **sub-unit 1A.3.1.**, ionic liquids are used as stabilizing agents or templates or reaction medium in the nanoparticle synthetic processes. For example, two ILs namely 1-dodecyl-3-methylimidazolium bromide [C_{12}mim]Br) and triethylamine acetate ([$NH(C_2H_5)_3$]OAc) were used as templates to fabricate ZnO/Ag_2O heterostructures by photochemical method to degrade organic dyes and antibiotics [191]. It was noticed that the growth of ZnO nanoparticles was dependent on the ILs. The IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate was employed to prepare Ag/ZnO nanostructured composites by a sonochemical method [192]. Synthesis of flower-like ZnO heterostructures containing spherical Ag nanoparticles with the assistance of poly(1-vinyl-3-butylimidazolium ascorbate) (P[VBuIm][As]), which is a redox-active poly(ionic liquid), was given by Dule and group in 2017 [193]. In this case, the poly(ionic liquid) acted as a shape director as well as a capping agent, moderator for Ag^+ reduction and assistant for spherical Ag NPs formation. However, the photocatalytic behaviour of these Ag@ZnO heterostructures is yet to be studied in organic pollutant/dye degradation reactions. Structures of some ILs that are reported to be used in the synthesis of Ag containing ZnO nanoheterostructure composites are given in **Fig. 1A.9**. In this context, it was aimed to investigate the effects of N-sulfonic acid functionalized ionic liquids for fabrication of Ag based ZnO nanocomposites for enhanced photocatalytic activity in the degradation of representative cationic dye MB dye and its mixtures with other dyes namely methyl orange (MO) and crystal violet (CV) under sunlight.

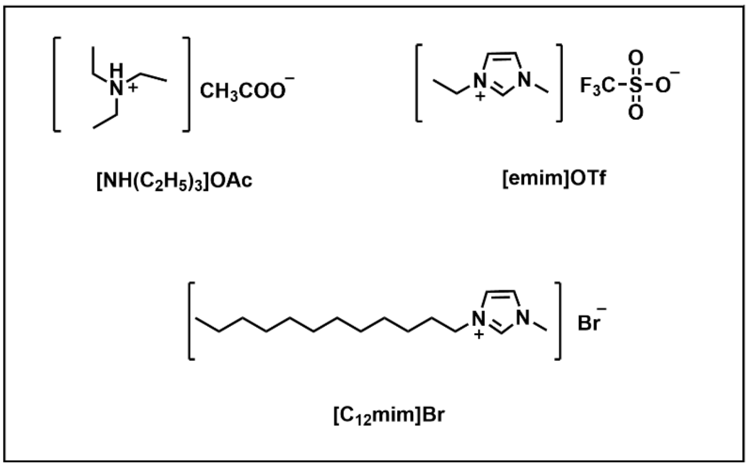


Fig. 1A.9: Structures of some ILs that are reported to be used in the synthesis of Ag containing ZnO nanoheterostructure composites.

1A.7. The objectives of the present study

From the discussion about ILs or organic salts in the previous sections, it is evident that they possess various exceptional features depending on the constituent ion-pair combinations as well as melting points to exist in liquid phase, for which they have been studied meticulously since long [194]. The liquid organic salts termed as ‘designer solvents’ are being used in numerous ways in today’s world, as their properties can be modified as per the requirement, where even a small change in their synthetic routes, choice of cation and anions, temperature, pH etc. can bring about a lot of differences in their characteristics [195]. Further, introducing specific groups to ILs/organic salts to develop ‘task-specific’ properties raised the utility of this class of materials to a whole new level, because such modifications not only generate new attributes but also supported the enhancement of intrinsic properties of ILs/organic salts [7, 9, 10]. The non-flammable and non-volatile natures of ILs contribute to minimizing the storage issues that emerge with using other volatile organic solvents or inflammable reagents. Despite being such a widely accepted domain, ILs sometimes accompany major challenges like moisture sensitivity or hygroscopicity, difficulty in recovery and reuse, non-biodegradability etc. [8, 196]. Such drawbacks negatively impact the applicability of ILs, which in turn lower the outcomes of the reaction processes. As an attempt to lower the restrictions that come along with using conventional ILs, initially group IIIA metals were introduced to ILs to develop halometallate ILs [31]. This modification was successful to some extent but contrary to expectations, the moisture sensitivity of some halometallate ILs still persisted. However, replacing the group IIIA metals with transition metals gave rise to moisture-stable and thermally stable halometallate ILs/organic salts [8]. Their Lewis acidity/basicity could be tuned accordingly, and their acidic properties could be enhanced by adding protic functional groups in their organic cations, which made them excellent choices as catalysts for the acid-catalyzed reactions, as briefly discussed in the **unit 1A.4**. As a broad class of pharmaceutically important N-heterocyclic compounds, the synthetic routes for quinazolines as well as quinazoline derivatives were reviewed in the **sub-unit 1A.4.1**. It was noticed that many of these synthetic processes required high temperature and prolonged reaction time to generate moderate to high yields of products. While a few methods were catalyst-free, some methods used expensive catalysts or excess amounts of oxidizing agents. Some processes had other major issues like difficulty in catalyst separation, no recyclability etc. Although few cases used Lewis acidic ILs of halometallate anion, no report was found where Brønsted-Lewis acidic halometallate organic salt was used to synthesize quinazolines or their derivatives. Considering the importance of quinazolines as well as their derivatives and the applicability of dual Brønsted-Lewis acidic halometallate organic salts in acid-catalysed reactions, we intend to develop them as recyclable heterogenous catalysts in the multi-component one-pot synthesis of 1,2-dihydroquinazolines under mild conditions.

Further, the modifications related to the traditional oxidant $KMnO_4$ was discussed in **sub-unit 1A.5.1** for the study of selective oxidation of primary/secondary alcohols to carbonyl compounds. Most of the methods in literature that used $KMnO_4$ in alcohol oxidations, either produced over-oxidized acidic products or required $KMnO_4$/solid support reagents in excess amounts. Some methods reported the modification of $KMnO_4$, where MnO_4^- anions were associated with the organic cations of ILs with varying alkyl side chains, as mentioned in the **unit 1A.5**. Although these permanganate-based organic-inorganic hybrid salts were used in various organic reactions, only a few instances of their usage in alcohol oxidations were observed. Apart from it, some of these hybrid salts are thermally unstable and decompose after a certain temperature and time limit. From the literature, it is seen that the organic cations used for preparation of the permanganate hybrids are of neutral character without the attachment of any acidic or basic substituent in their structures. In this context, there is a scope for further improvement of their hydrophilic/hydrophobic nature, thermochemical stability as well as oxidative properties by tethering acidic functionality to the organic cations, which would provide strong binding interactions between the ion-pairs of hybrids involving intramolecular electrostatic as well as H-bonding interactions. Similarly, as discussed in the **section 1A.5.2.**, not many reports on the selective oxidation of organic sulfides to sulfoxides by permanganate-based organic-inorganic hybrid salts are available in literature. In this regard, sulfonic acid functionalized cyclic/acyclic ammonium permanganate hybrids could be developed as recyclable internal oxidants in the selective catalytic oxidations of alcohols to carbonyl compounds and organic sulfides to sulfoxides.

Moreover, the significance of degradation of organic pollutants and literature on Ag based ZnO nanocomposites were reviewed in **unit 1A.6**. In this case also, very few reports on the degradation of organic pollutants by Ag/Ag_2O/ZnO nanocomposites were found and there was hardly any report on the fabrication of Ag/Ag_2O/ZnO assisted by functionalized ILs, as per our scope of knowledge. Considering the stabilizing effects on the growth of nanoparticles in ILs, as discussed in the **sub-unit 1A.3.1.**, development of Ag/Ag_2O/ZnO nanocomposites assisted by sulfonic-acid functionalized organic salts with varied ammonium cations could be done to explore their photocatalytic efficiency under visible light to degrade dye molecules.

1A.7.1. 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.

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Chapter 1B

Materials & Methods

1B.1. General Information

This chapter primarily overviews the general spectroscopic as well as analytical techniques that were engaged to characterize the synthesized N-SO_3H functionalized halometallate organic salts, organic-inorganic hybrids of permanganate salts and Ag based nanocomposites of ZnO prepared by acidic organic salts assisted reactions. FT-IR spectroscopy provided information about the vibrational frequencies of specific bonds and functional groups present in the synthesized compounds. Melting points of known and unknown organic products were recorded. Thermogravimetric analyses (TGA) were done to understand the thermal behaviour of the chlorometallates and permanganate based organic salts. The Brønsted and Lewis acidic strength of the chlorometallates were checked using UV-Visible Hammett plots and FT-IR analysis with pyridine as probe molecule, respectively. Analysis of the oxidized organic products were done using High-Performance Liquid Chromatography (HPLC) and Gas Chromatography-Mass Spectrometry (GC-MS) techniques. Specific surface area and pore size of the Ag/Ag_2O/ZnO nanocomposites were investigated using Brunauer-Emmett-Teller (BET) analysis. The photocatalytic dye degradation reactions were monitored using UV-Visible spectroscopy. To confirm the structural compositions of the synthesized materials, further characterization was done by using PXRD, Raman, UV-Visible DRS, SEM, EDX, TEM, elemental mapping, XPS etc. techniques. Theoretical study of the 2-methyl-1,3-disulfoimidazolium permanganate salt was also done.

1B.2. Materials used in this study

All the required chemicals used in these studies were purchased from renowned commercial suppliers such as MERCK, TCI chemicals, Alfa Aeser and Loba Chemie. The chemicals were received in pure state and used directly without any extra purification.

1B.3. Analytical techniques of characterization

The following analytical techniques were used to characterize the synthesized organic salts and organic products:

1B.3.1 Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra of all the samples, liquid as well as solid, were recorded on Perkin Elmer MIR-FIR FT-IR spectrophotometer. The presence of functional groups like -OH, C=O, $-SO_3H$, etc. could be identified by recognizing characteristic vibrational frequencies of the specific bonds present in these groups. The fingerprint region (2000-450 cm^{-1}) gave information about existence of various functional groups in the synthesized compound by showing characteristic stretching and bending vibrations of organic compounds or organic cations. Stretching vibrations for O-H, N-H, C-H etc. bonds were found in the 4000-2500 cm^{-1} region of the FT-IR spectra. Presence of metallic bonds was observed by studying vibrational frequencies in Far-IR region (500-300 cm^{-1}). Using pyridine as probe molecule, IR spectra was employed to evaluate the Lewis acidity of the prepared chlorometallates. Absorption bands around 1480 to 1490 cm^{-1} were displayed for pyridine coordinated Lewis acidic sites, while peaks for Brønsted acidic pyridinium ion formation were observed around 1530-1550 cm^{-1} [1].

1B.3.2. Nuclear Magnetic Resonance (NMR) spectroscopy

All the NMR spectra (^1H and ^{13}C) included in this study were recorded on JEOL 400 MHz spectrophotometer (δ in ppm) in different solvents. Radiofrequency of 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR were used. NMR spectra of the reported ILs/organic salts were taken in DMSO-d_6 solvent. NMR spectra of the organic products such as the synthesized 1,2-dihydroquinazoline products and the sulfoxide products were taken in $CDCl_3$ solvent.

1B.3.3. CHN elemental analysis

The CHN analysis of the prepared chlorometallate organic salts (**Chapter 2**) were done using CHN PerkinElmer 20 analyser, to know the amount of C, H and N in the samples.

1B.3.4. Melting point measurements

The melting point measurements for the organic products, 1,2-dihydroquinazolines and sulfoxides (**Chapter 2 & 4**), were taken using BUCHI M-560 digital melting point and compared with the reported literatures.

1B.3.5. Thermo-gravimetric analysis (TGA)

Thermogravimetric analysis of the prepared materials was done to know their thermal stabilities within a temperature range of R.T.-600 °C, using a Shimadzu TGA-50 analyser. TGA analysis of the prepared samples gave us an idea about the moisture content in the organic salts. It also allowed us to compare the difference in thermal behaviour of the parent organic salts and synthesized metal-containing organic salts.

1B.3.6. Powder X-Ray Diffraction (PXRD) analysis

PXRD patterns of halometallate organic salts (**Chapter 2**) and permanganate hybrid (**Chapter 3**) were recorded using Rigaku–Multiflex instrument using a nickel filtered Cu K (0.15418 nm) radiation source and scintillation counter detector. PXRD patterns of permanganate hybrids (**Chapter 4**) and nanocomposites (**Chapter 5**) were obtained from 9KW Powder X-ray diffraction system (make: Rigaku technologies, Japan, model: Smart lab). PXRD analysis provided us with information about the structural composition of the prepared solid samples. It also confirmed the incorporation of metal chlorides/oxides in the synthesized organic salts (**Chapter 2-4**) and suggested the formation of Ag as well as Ag_2O in the Ag/Ag_2O/ZnO nanocomposites (**Chapter 5**). In addition, PXRD analysis was used to verify the selected area electron diffraction (SAED) pattern for the nanocomposites for distinct diffraction planes.

1B.3.7. Raman Spectroscopy analysis

Raman Spectroscopy analysis of the halometallate salts (**Chapter 2**) was performed on Horiba LabRAM HR spectrophotometer furnished with a He-Ne laser of excitation wavelength of 633 nm. The Raman spectra of all the permanganate hybrids and nanocomposites (**Chapter 3-5**) were recorded on RENISHAW BASIS SERIES spectrophotometer furnished with a green argon-ion laser of excitation wavelength of 514.5 nm. Raman spectra of the samples gave us information about the structural fingerprint of the samples by displaying characteristic vibrations for Raman active modes.

1B.3.8. UV-Visible Spectroscopy analysis

The Hammett acidity study of the prepared halometallate salts as well as the parent organic salt and the degradation study of organic dyes were done using a Shimadzu UV 1800 spectrophotometer. The Brønsted acidic strength of the organic salts (**Chapter 2**) was determined through comparative UV-visible spectra of 4-nitroaniline in water containing the three halometallates as well as the parent ionic salt. The spectra were obtained in descending order as calculated from Hammett acidity function H° values using **Equation (1B.1)**, as per the standard methods [2, 3], where 4-nitroaniline was employed as a basic indicator to determine the acidity of organic salts.

$$H^{o} = pK(I)_{aq} + \log[I]/[IH]^{+} \qquad \textbf{Equation (1B.1)}$$

Here, pK(I)aq represents pKa value of the basic indicator in aqueous solution.

The calculated values of H° from this equation was found to be decreased for an increasing trend in the acidity of the organic salts.

1B.3.9. UV-Visible Diffuse Reflectance Spectroscopy (DRS) analysis

The UV-Vis DRS analysis was carried out to get the electronic spectra of the solid samples (halometallate salts, permanganate hybrids, nanocomposites) by using Shimadzu UV 2450 spectrophotometer with diffuse reflectance apparatus. The spectra were recorded within 200-800 nm wavelengths. Firstly, UV-DRS of $BaSO_4$ was run as a blank sample to take it as a reference. Then, sample measurement was done by grinding 20-25 mg sample with 0.5 g of $BaSO_4$ and spreading this mixture in a uniform manner on the sample plate. The spectra showed absorption peaks for specific electronic transitions at certain wavelengths. Additionally, the optical band-gap values for the synthesized nanocomposites were calculated using the following equation [4]:

$$(\alpha h\nu)^2 = A(h\nu - Eg) \qquad \textbf{Equation (1B.2)}$$

Where, α is the correlation of absorption efficiency, h is Planck's constant, ν is the frequency of light, A is a constant, Eg is the optical energy of bandgap [4]. Optical bandgap Eg for a material could be obtained by plotting a graph of $(\alpha h\nu)^2$ $(eV/cm)^2$ vs. energy of photons, hν (eV). From the curve, a straight-line tangent was drawn to the X-axis, where the intersecting point of the tangent and X-axis gave the bandgap energy of the material.

1B.3.10. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis

The SEM images provided us with information about the surface morphologies such as the size and shape of the surface granules as well as the agglomeration of granules on the material surface. EDX images indicated the presence of all the constituent elements in the synthesized materials. Elemental mapping images displayed the distribution of elements in the samples. SEM images and EDX images of the halometallate salts and permanganate hybrids were recorded on JEOL JSM-6390LVSEM equipped with EDX analyser (**Chapter 2-4**). The same instrument was used to record the elemental mapping images of the permanganate hybrid salt (**Chapter 3**). SEM images, EDX images and elemental mapping images of the nanocomposites (**Chapter 5**) were recorded on Zeiss Sigma 300.

1B.3.11. Transmission Electron Microscopy (TEM) analysis

TEM analysis was carried out to know the internal structures of the nanocomposites (**Chapter 5**). Electric beams of high resolution were used to know the shape and size of internal particles/granules in nanoscale. It also exhibited the distribution manner of particles/granules within the sample. It displayed the lattice fringes of nanoparticles from which the d-spacing of reflection planes could be calculated. It also exhibited the selected area electron diffraction (SAED) pattern for distinct diffraction planes of nanocrystals. The TEM analysis of the nanocomposites (**Chapter 5**) was carried out using TEM-200KV (make: FEI Company, USA; Model No. FEI 200KV TEM model Tecnai G2 F20 S-TWIN).

1B.3.12. The Brunauer -Emmett-Teller (BET) analysis

The BET analysis was done to know the specific surface area and pore size of the nanocomposites (**Chapter 5**). It also indicated the porosity of the materials. The distribution of pore-size could also be studied by this analysis. The BET isotherm plots of the nanocomposites for N_2 gas adsorption-desorption at 77.3 K were obtained from Quantachrome NovaWin ©1994-2018, Quantachrome Instruments v11.05, Nova station B instrument.

1B.3.13. X-Ray Photoelectron Spectroscopy (XPS) analysis

XPS analysis of the nanocomposites was carried out to know the elemental composition and chemical state of the materials in the nanocomposites. The XPS analysis of the Zn, Ag and O elements in the nanocomposites (**Chapter 5**) was carried out using Thermofisher Nexsa XPS instrument (source: Al Kα, vacuum: 10^{-8} mbar, pass energy: 200 eV, dwell time: 10 ms, binding energy scale: 0-1350)

1B.3.14. High-Performance Liquid Chromatography (HPLC) analysis

Analysis of the oxidized products of primary/secondary benzyl alcohols was (**Chapter 3**) carried out by High-performance Liquid Chromatography (HPLC) (Waters 2489 UV/Visible detector) using C_{18} reverse phase column and UV detector at 254 nm.

Water and acetonitrile in a 1:1 mixture was used as mobile phase with a flow rate of 1 mL/min for 15 minutes of retention time. The conversion of aromatic alcohols to aldehydes and ketones in the reaction processes could be calculated by **Equation 1B.3**.

$$\% \text{ Conversion of aromatic alcohols} = [(C_0 - C_n)/C_0] \times 100 \qquad \textbf{(Equation 1B.3)}$$

In this equation, C_n is the concentration of aromatic alcohols measured at time t, and C_0 is the initial concentration of alcohols prior to reaction [5].

1B.3.15. Gas Chromatography-Mass Spectrometry (GC-MS analysis)

Analysis of the sulfoxide products (**Chapter 4**) was carried out by Gas Chromatography-Mass spectrometry (GC-MS) on Perkin Elmer Clarus 680 with a 5MS (methyl polysiloxane) column (60.0 m × 250 µm) using He as carrier gas (flow rate 1 mL/min). The injector temperature and source temperature were 250 °C and 160 °C, respectively, while the column temperature was 60-300 °C. The GC oven was operated with a 60 °C initial temperature for 1 min, raised up to 200 °C with a rate of 7 °C/min (hold time 3 min), which was further raised up to 300 °C with a rate of 10 °C/min (hold time 5 min).

1B.3.16. Theoretical calculations

Density functional theory (DFT) method, with Becke three-parameter exchange and Lee-Yang-Parr correlation (B3LYP) functional and the 6-311++G(d,p) basis set, was used for electronic structure optimization of each species involved in the reaction mechanism of alcohol oxidation (**Scheme 3.3, Chapter 3**) along with theoretical calculations of other parameters [6, 7]. The Gaussian 09 software package was utilised to perform all the DFT calculations [8].

1B.4. Bibliography

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