Chapter-1A

General Introduction and Review of Literature

1A.1 Ionic liquids and their significance

Ionic liquids (ILs) are salts containing organic cations and organic or inorganic anions which exists in liquid state with melting point typically below 100 °C, considering the boiling point of water as the point of reference. They are made up by pairing of organic cations with organic or inorganic anions. Poor coordination of the constituent ion-pair results in liquid state of these organic salts. A lot of names have been used to depict ionic liquids like room-temperature ionic liquid (RTILs), molten salt, liquid organic salt, fused salt, liquid electrolytes, ionic melts, ionic fluids, etc. [1]. Physical properties of these ILs like thermal stability, low vapour pressure, melting point, density, viscosity, solubility, conductivity etc. are determined by the combinations of organic cations and anions as well as different substituents added to the constituent ions [2]. Ionic liquids are also termed as designer solvents because of their attractive tuneable physicochemical properties including low vapour pressure, non-volatility, ability to solubilize organic, inorganic, polar, nonpolar species etc., forming biphasic solvent system, acting as dual-solvent catalyst at the same time, acting as co-catalyst and because of possessing large electrochemical window, they can be used as electrolytes for many studies [3-6].

Introduction of functionality into the cation or anion of ILs allows specialized properties into them which in turn provides specificity for special reaction or applications [7]. A distinctive term, functionalised ionic liquids (FILs) is used for such class of ionic liquids. Functional groups are covalently tethered into the cation or anion or both according to need of the reaction and service it is expected to provide. Designing ionic liquids by adding proper functionality into the constituent ion-pairs can tune them into homogeneous, heterogeneous, or multiphasic behaviour of the catalysts [8-10]. Functionalization of the ILs can be done by incorporation of Brönsted acidic functional groups (e.g. -COOH, -SO$_3$H), basic functional groups into the ion pair, incorporation of Lewis acidic complex metal halide anions etc. as per necessity to run a chemical reaction. The development of ionic liquids with objectives of providing structural stability, negligible catalyst leaching through proper functionalization and introduction of coordination ligands serve the purpose of carrying out homogeneous reaction with nominal catalyst loss. Shreeve et al. [11] developed monoquaternized 2,2′-biimidazolium-based ionic liquids with non quaternized nitrogen centre to serve as strong coordination centre for palladium catalyst to perform Suzuki cross coupling reactions. This IL worked as efficient solvent-catalyst system without leaching of the Pd cation due to its strong

coordinating ability and was recycled at a minimum for 10 times without any remarkable loss in catalytic activity. The literature review [12, 13] on different ionic systems disclose enormous scope for designing of task specific ionic liquids (TSILs) with proper attachment of functional groups to the ion-pairs and generation of organic-inorganic hybrid materials of complex metal anionic speciation with organic cations.

1A.2 Understanding functionalization in ionic liquids and their need in task specific reactions

Functionalization imparts specific properties into the ionic liquid. The most pivotal type of functionalization is done by addition of acidic or basic functionality into the ILs. The following sub-units will provide a brief information regarding functionalized acidic and basic types of the ILs.

1A.2.1. Acidic ionic liquids

An acidic ionic liquid can be either Lewis, Brönsted or mixture of both Brönsted and Lewis acid [14]. The Lewis acidic ionic liquids (LAILs) exhibit acidity because of electron accepting capacity present in them (**Fig.1A.1**). Halometallate ILs are an important class of Lewis acidic ionic liquids [15]. This section gives a concise information about Brönsted acidic ionic liquid (BAILs) by considering the objectives of this thesis for synthesis of such type of ILs and IL based materials.
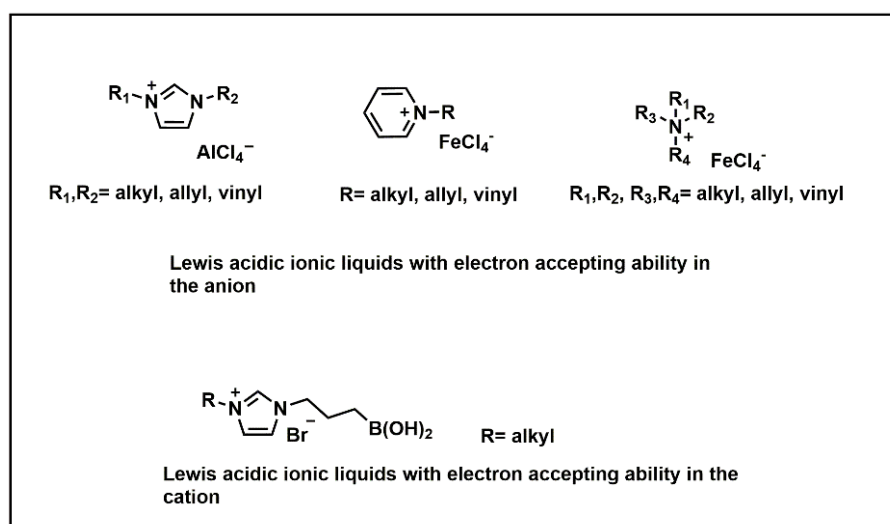
Fig.1A.1 Examples of Lewis acidic ionic liquids.

In 1923, Johannes Nicolaus Brönsted and Thomas Martin Lowry proposed a theory 'Brönsted−Lowry theory'. A compound is said to be Brönsted acidic nature when it donates a hydrogen ion (H^+). Based on this concept, Brönsted acidic ionic liquids (BAILs) are those groups of ionic liquids that can donate proton. The BAILs are classified into 5 groups (**Fig. 1A.2**) based on the location of releasable proton in the structure of ILs. The first one is 'Protic Acidic Ionic Liquids with Acidic Hydrogens on Cation.' In this class of ionic liquids, the acidic hydrogen is located on the cationic counterpart [16-24]. The second one is 'Protic Acidic Ionic Liquids with Acidic Hydrogens on Anion.' This class will have releasable proton residing in the anionic counterpart of the ionic liquid [25-28]. The third class is 'Protic Acidic Ionic Liquids with Acidic Hydrogens on Cation as well as on Anion.' This class of ionic liquid have protons residing on both the anion as well as cation [29]. The fourth class is 'Brönsted Acidic Ionic Liquids with Acidic Hydrogens on a Functional group.' This class of ionic liquids consists of functional groups with acidic proton tethered into either the cation or anion [30,31]. The fifth class is 'Brönsted Acidic Ionic Liquids with Acidic Hydrogens on Functional Groups and on an Anion or Cation.' This class of ionic liquids consists of functional groups with acidic proton tethered into both the cation as well as anion [32-34].
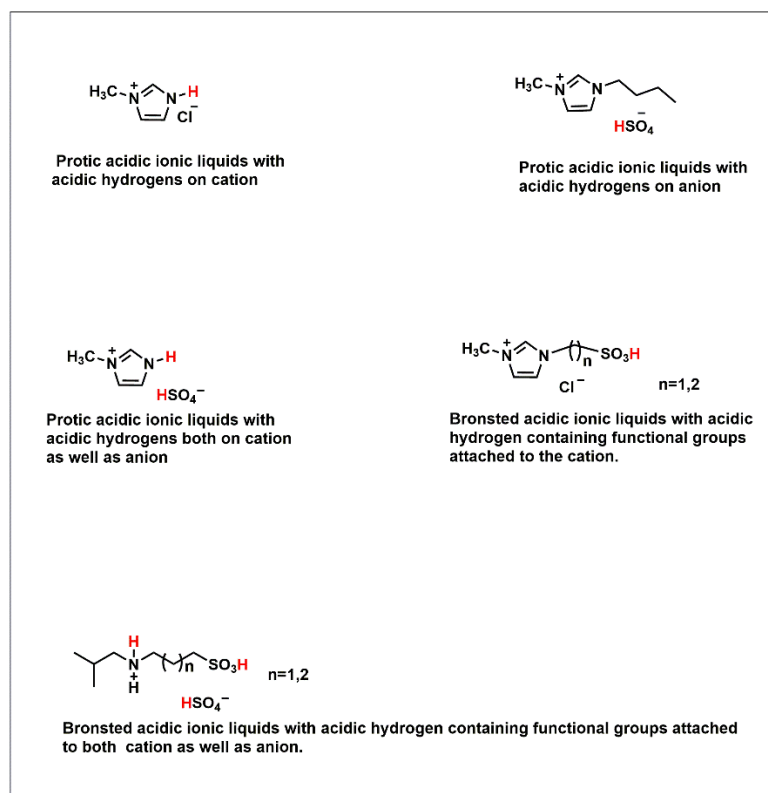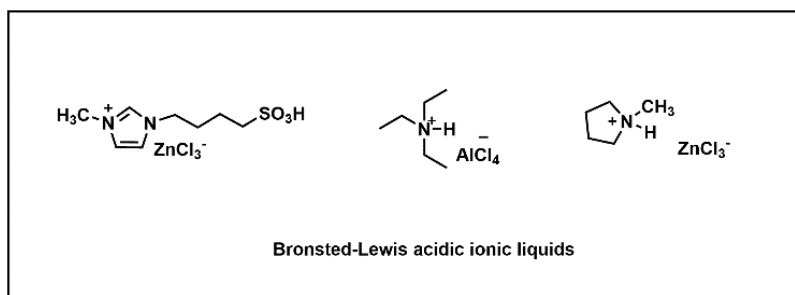

Fig. 1A.2 Examples of Brönsted acidic ionic liquids.

Thus Brönsted-Lewis Acidic Ionic Liquids (BLAILs) are the group of acidic ionic liquids consisting of both Brönsted and Lewis acidic groups (**Fig. 1A.3**). These are task oriented ionic liquids for uses in catalytic reactions which call for the need of both types of acidity [35].


Fig. 1A.3 Examples of Brönsted-Lewis acidic ionic liquids.

1A.2.2 Basic ionic liquids

The other type of functionalized IL is basic ionic liquids (BILs) and generally the anions present in the ionic liquid imparts basic character into them. The first stable basic ionic liquid 1,3 dibutylimidazolium hydroxide was reported by Seddon et al.in 2004 [36]. The anions those are commonly used for synthesis of basic ionic liquids are lactate, formate, acetate, dicyanamide anion, hydroxide, fluorinated carboxylates, fluorinated sulfonates, imides, halometallates etc. have been employed (**Fig.1A.4**). The basic ionic liquids with dicyanamide anions as phosphonium salts are preferably used for many applications because of their low viscosity. Numerous beneficial properties like solubilizing properties as well as catalytic properties are imparted due to the presence of basic anions. Apart from the ILs with basic anions, it is also possible to incorporate basic site into the organic cation which is seen to increase thermal stability in the ILs compared to the ionic liquids with basic anions [37]. Some examples of the basic ionic liquids are mentioned in the **Fig.1A.4** [38-41]. They offer an alternative solution to traditional basic reagents which have drawbacks like use of excess number of reagents, corrosiveness, miscibility with non-polar solvent, non-recyclability etc. The BILs are environment friendly sustainable base catalyst with various benefits like water and air stability, easy recovery and reuse, high catalytic efficiency etc [42]. In 2005, Ranu et al. synthesized basic ionic liquid [bmIm]OH and used it in base catalysed Michael addition reaction with a very convenient environmentally friendly procedure in comparison to the conventional procedure using stoichiometric amount of strong inorganic bases [43]. Various BILs are used as catalysts for reactions

such as Knoevenagel condensation, condensation of aldehydes and ketones with hydroxylamine, synthesis of quinolines, pyrroles, and many more heterocyclic compound or intermediate synthesis etc. [44-47].
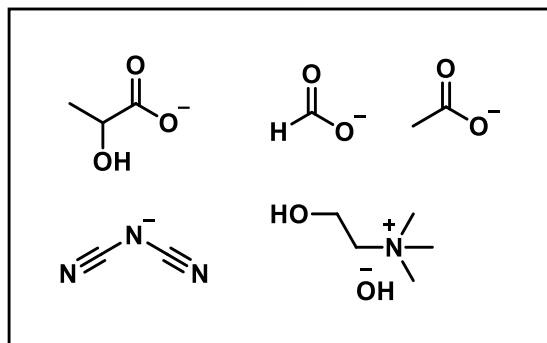
**Fig. 1A.4**. Examples of basic ionic liquids and few anions used for preparation of basic ionic liquids.

1A.2.3 Task-specific functionalized ionic liquids

Task specific ionic liquids (TSILs) are those ionic liquids which are designed with composition depending as per the need of users [48]. Tuneable properties by deciding suitable choice of the cations and anions make them beneficial candidates for various chemical synthesis [49]. Task specific ionic liquids (TSILs) or task oriented ionic liquids (TOILs) are the types of ILs that are designed to display specific reactivities on incorporation of functional group specifically utilised for advancement of the reaction [50]. In the TSILs, the functional groups are covalently attached to either cationic or anionic counterpart or both. The first idea of designing thiazolium functionalized task specific ionic liquid and its function as both catalyst and solvent for benzoin condensation was illustrated by Davis and co-workers [51]. The TSILs have added superiority compared to other supported catalyst because the liquid state provides them with large active surface area for the reactants to react [48]. Moreover, the motility and potential activity of the liquid state of the TSILs is always a beneficial point to be noted [30]. Indulgence of required chemical, physical, and biological properties into the TSILs aids in conducting reactions in different fields of research. Functionalization into the ILs based on specific task results in modification of certain parameters like polarizability, polarity, acidity, basicity, hydrogen bonding etc. Moreover, the functional group tethered into the IL acts as the active reaction site that catalytically activate the reactants for progress of reaction.

Constructing ionic liquids with covalently attached functional groups are also found to achieve certain tasks like catalyst surface modifiers, catalysis, chiral induction, organic synthesis, electrochemical applications, etc. [48]. An elaborative idea on designing Brönsted acidic ionic liquids and their application, is presented in the following paragraph.

Many catalytic studies were performed in which Brönsted acids are added in IL media [52]. Although using ionic liquid as reaction media had many advantages but the possibility of outgassing of the dissolved Brönsted acid is a significant drawback both in terms of green chemistry principles and health related hazards. So, the limitations of addition of strong acids in volatile organic solvents was not solved by addition of strong acid using IL as media. Acknowledging the drawbacks related with addition of strong acids to ILs, TSILs were synthesized with alkane -SO_3H functional group covalently tethered to one of the ions or both. Ohno et al. in 2001, synthesised ionic liquids comprising imidazolium cations and covalently attached sulfonate or sulphonamide groups as anion [31]. Use of such TSILs decreased the risk of release of strong volatile acidic fumes. While synthesizing such Brönsted acidic functionalized TSILs, the choice of acid for generation of ILs must be kept in mind as anions like HPF_6^- and HBF_4^- are hydrolytically unstable and may lead to outgassing of volatile HF [46]. Practically using such TSILs can serve as an effective alternative because these can act as both acid catalyst and reaction media at the same time [51]. Cole et al. synthesised BAIL systems and utilised them as dual catalyst/solvent for Fischer esterification, dehydrocoupling of alcohols, and Pinnacol rearrangement [30] [**Scheme 1A.1**]. Forbes et al. in 2004, synthesized alkane sulphonic group tethered phosphonium based ionic liquid and utilised for Fischer esterification reactions. It was observed that presence of water as reaction media with the synthesized TSIL catalyst counterintuitively increases the yield of product. They proposed that the presence of water rendered the sulphonic acid proton of the synthesized TSIL to be more chemically accessible during the reaction like the activity of Amberlite and Dowex type acid resins [53] [**Scheme 1A.1**]. Researchers have synthesized many acid and base functionalized task specific ionic liquids and utilized them in various organic reactions like Mannich reaction [54,55], Aza-Michael reaction [56], Knoevenagel condensation reaction [57], Diels–Alder Reaction [39,58], esterification [59], polymerization [60], alkylation [61,62], acylation [63], carbonylation [64], aldol condensation [65,66], and pinacol rearrangement [67,68], cleavage of ethers [69], Beckmann rearrangement [70], oxidation of alcohols [71], nitration [72,73], Koch reaction [74]. All these reactions show

good to excellent yields with easy recyclability up to many cycles. Apart from having catalytic applications by acidic/basic TSILs, these are used for other applications in diverse field. Nevertheless, tuning of ionic liquids properties and using them as substitute for organic solvents has been a great objective for researchers in the field of chemistry [75]. One of such research objectives is use of ionic liquids as an alternative to organic solvent in metal extraction from industrial wastewater [76,77], **(Fig 1A.5)**. This field has achieved a lot of success till now and designing TSILs with inbuilt extractants or chelators has played a terrific role in extraction experiments [78]. An elaborate discussion about this is provided in the upcoming sections.
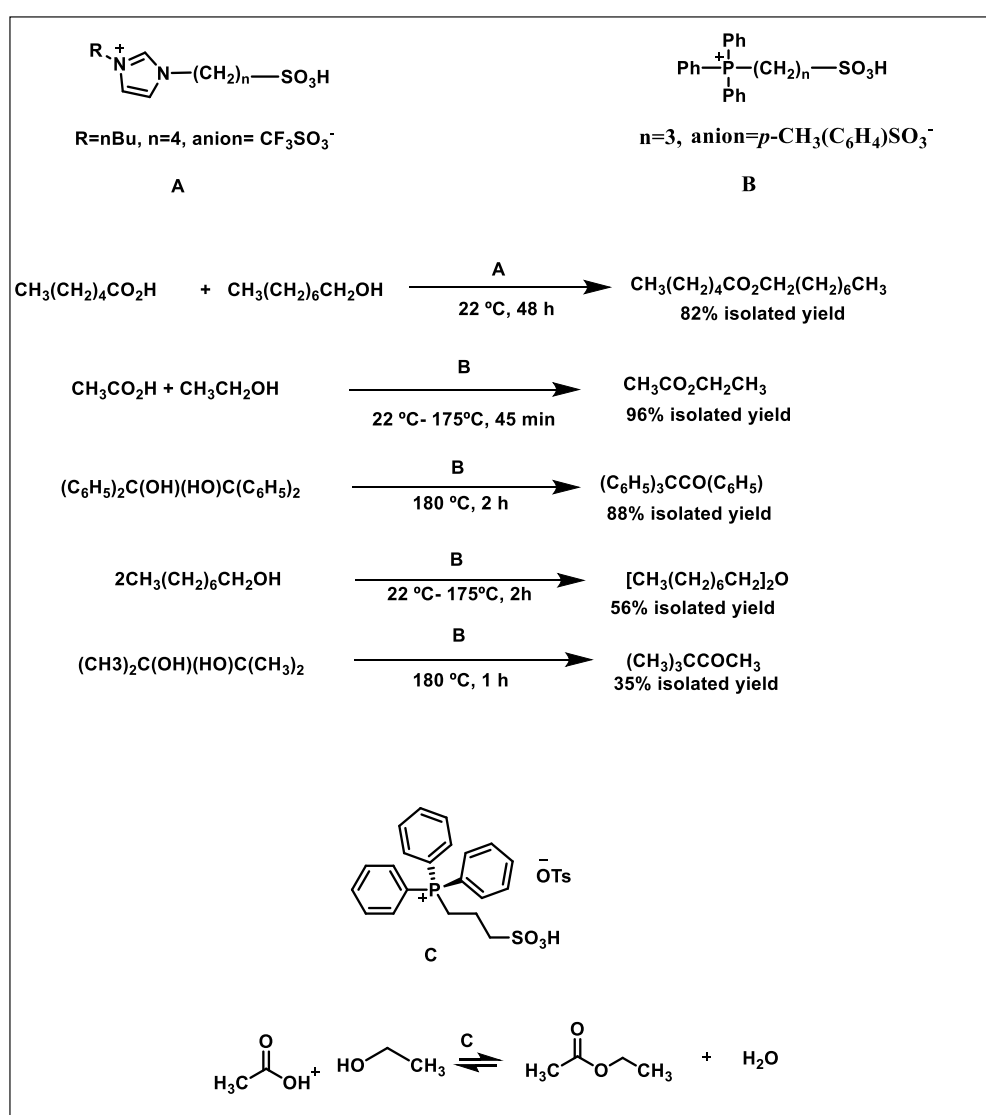
Scheme 1A.1 Representative reactions catalyzed by TSILs (A and B) [Cole et al. [30]]; Representative reaction of Fischer esterification catalyzed by TSIL (C) [Forbes et al. [53]].
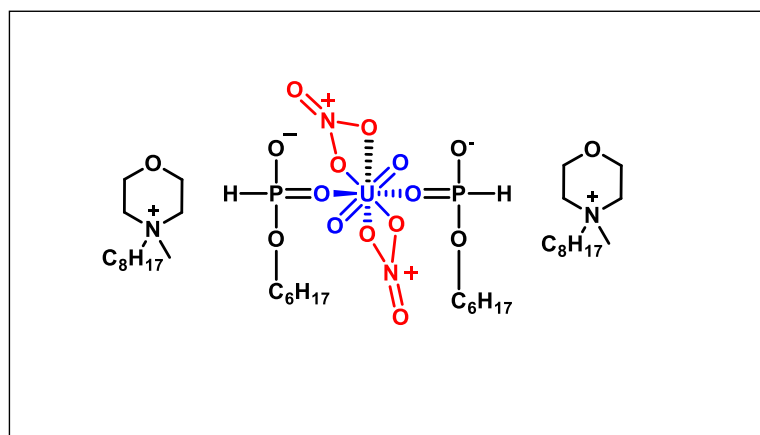
Fig. 1A.5 Ionic liquid based on H-phosphonate anions synthesized and used by Zarrougui et al. [77] for separation of uranium (VI) from transition metals.

1A.3 Need of heterogeneous catalysts made of ionic liquid and understanding polyoxometalates (POM) as anion

One important aspect of using ionic liquid as heterogeneous catalytic system is the immobilization of ionic liquids in various supports. Immobilization transfers the task specific properties of IL into the surface of heterogeneous material and with increase in surface area of active sites reduces the quantity of expensive ionic liquids as catalyst along with easy separation for reuse [6]. The immobilization of ILs into supports is mainly done through formation of covalent bond with the surface of support or by secondary interactions to generate supported liquid phases (SLPs), which does not involve covalent bond interaction between the ionic liquid and the support [79]. Despite all that, immobilization of the IL is also observed to show a lot of drawbacks. In many cases, supports like zeolite was observed to get structurally destroyed while immobilization is done with task specific ionic liquids [80-82]. Furthermore, there are also evidences of heterogenization of IL involving covalent bond formation between the anion of ionic liquid with the functional groups present in the surface of structured supports of MCM (Mobile Composition of Matter) family that showed destruction of the supports along with reduction in acidity of the ionic liquid [83]. Here comes the need for synthesizing ionic liquid based solid catalyst that does not bring about any destruction in the resultant structure. Integrating the ion-pair of organic cations with polyoxometalates (POMs) counter anions leads to generation of organic-inorganic hybrids of ionic liquid and polyoxometalate with unique physical and chemical properties. These properties can be tuned as different types of interaction comes into existence according to the functional

groups attached to ionic liquid cation that will be combined with the POM anion. Thus, modifying the ionic liquid composition into ionic liquid based-polyoxometalate not only brings about some distinctive characteristic properties in each type of hybrid but also overcomes the limitations of immobilization faced with ionic liquids with supports. It was observed that these hybrids show good results as phase transfer catalysts [84]. The heterogeneous nature introduced in such hybrids was observed to show excellent performance in catalytic reactions [84].

Polyoxometalates (POMs), are a diverse family of polynuclear metal-oxide compounds with variety in magnetic [85,86], electronic [87-89], catalytic [90-92] and optical [91,93] properties. The structural stability and high activity combined with low toxicity have extended their applications in biology [94], electrochemistry [95], nanomaterials [96], and surface science [97]. Structurally, POMs are anionic molecular metal-oxide building blocks. This class of metal-oxide clusters comprises of diverse structures in terms of size and elemental composition [98]. The metals present in POMs are mainly the early transition metals in their highest oxidation state (e.g., M = V, Nb, Ta, Mo, W). However, this class of compounds may also contain a variety of heteroatoms (e.g., X = P, As, Si, Ge), apart from only early transition metals [99]. POMs can be classified into three classes depending on their structure:

i. Heteropolyanions

These are polyatomic clusters of metal-oxide that include heteroanions such as SO_4^{2-} and PO_4^{3-}. The two basic structural forms of heteropolyanions are Keggin and Wells-Dawson structures. The general formula for Keggin structure is $[XM_{12}O_{40}]^{n-}$ and Wells-Dawson structure is $[X_2M_{18}O_{62}]^{n-}$, where (X= tetrahedral template, M= addenda atom W or Mo, O represents oxygen) [98]. Following results are proposed from X-ray analysis of the structure of α-Keggin anion i.e. anion of 12-phosphotungstic acid: A regular tetrahedron is surrounded by 4 oxygen atoms at the corners with heteroatom X at the centre [100]. In a similar way, a distorted octahedron is surrounded by 6 oxygen atoms at the corners with addenda atom, M at the centre. The heteroatom X is centrally positioned in XO_4 tetrahedron surrounded by 12 MO_6 octahedral units connected via neighbouring oxygen atoms of each unit. The 12 addenda atoms of the MO_6 units are connected by a total of 24 bridging oxygen atoms. The 12 MO_6 octahedron units are organized in four groups of 3 MO_6 units. In a group of 3 MO_6 units, two oxygen atoms from each octahedra are shared

with the neighbouring two units. From each group of $3MO_6$ unit, one oxygen atom one group is shared with the centrally positioned XO_4 tetraheron. The whole symmetry with centrally located XO_4 unit and four groups of 3 MO_6 octahedron gives an overall tetrahedral symmetry, [**Fig.1A.6(a)**] [100]. The other basic structure is the Wells-Dawson structure. Removal of 3 MO_6 octahedra units from the α-Keggin structure results in lacunary α-Keggin lacunary fragments, here lacunary means missing fragments. Combining two such α-Keggin lacunary fragments results in Dawson model $[X_2M_{18}O_{62}]^{n-}$ [**Fig. 1A.6 (b)**] [101].
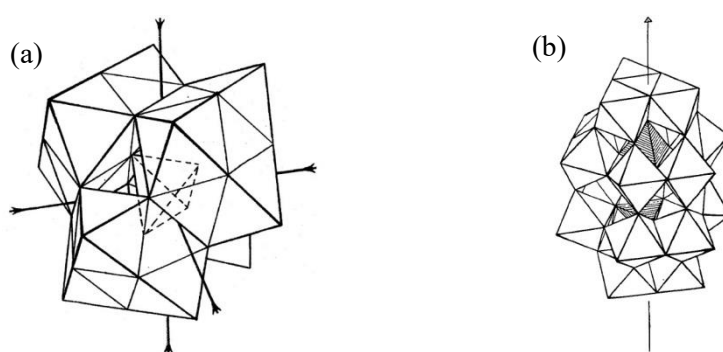
Fig. 1A.6: (**a**) Structure of $PW_{12}O_{40}^-$ anion; Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 144(851):75-100, 1934 (**b**) Structure of 9(18)-tungstophosphate anion $[P_2W_{18}O_{62}]^{6-}$; Acta Crystallographica, 6(2):113-126, 1953.

ii. Isopolyanions

This class of POMs comprises of only metal and oxygen in their structural framework without any heteroatom. Lindqvist structures are the most common isopolyanions with general formula $[M_6O_{19}]^{n-}$,(M = Mo, W (n = 2); Ta, Nb (n = 8) [102,103]. Because of the absence of heteroatom/heteroanion, their stability is comparatively less than heteropolyanion counterparts [104]. Nevertheless, their physical properties like as high charges and strongly basic oxygen surfaces makes them interesting units to be used as building blocks for various applications [98].

iii. Molybdenum blue and Molybdenum brown

Molybdenum blue (Mo-blue) and Molybdenum brown (Mo-brown) are reduced POM clusters with very high nuclearity. Partial reduction of acidified Mo(VI) centres to Mo(V)

generated a family of mixed valance reduced molybdenum POM clusters which are deep blue in colour [105,106]. Müller et al. reported the structural characterization of the cluster {Mo$_{154}$}; the big wheel [107]. Modifying the pH, amount of reducing agent and incorporation of acetate ligands promotes the formation of a {Mo$_{132}$}(Mo-brown) spherical ball-like cluster [98].

1A.4 Organic -inorganic polyoxometalate based hybrids

Scheming and synthesizing various organic-inorganic hybrid material incorporates superior properties of both organic and inorganic units alongside properties better than both the units. The possibility of generating hybrids with tunable properties has captivated attention of researchers towards their development. Customizing properties of hybrid for executing a specific application is one of the greatest benefits of developing such hybrids. Based on the interaction of POMs with the organic component, the POMs based organic-inorganic hybrids can be classified into two classes: Class I and Class II hybrids.

i. **Class I hybrids** are those in which the interaction between organic and inorganic units takes place via non-covalent interactions (electrostatic interactions, H-bonding or Van der Waals etc.). The association of the organic cation to the POMs occurs due to anionic character of the POMs [92]. The charge-charge interactions of anionic POMs occur with organic cations like cationic surfactants, quaternary ammonium cations and ionic liquids etc. [6,108-115]. The ionic liquid-polyoxometalate hybrids synthesized in this thesis are a kind of **Class-I** type of organic-inorganic hybrids.

ii. **Class II hybrids** are those in which the interaction between organic and inorganic units takes place via covalent interactions (covalent or iono-covalent bonds). The association can occur by attaching the organic ligand directly to the metallic centre via organic ligand substituting an oxo group of the POMs. Moreover, covalent bond formation can occur between electrophilic groups present on the organic ligands with the nucleophilic oxygen atoms present on the surface of the POMs.

The proposed research work in this thesis is mainly centred on designing **Class-I** type of organic-inorganic IL-POM based hybrids and so the discussion is not expanding further on **Class-II** types.

1A.5. Importance of cationic counterpart in organic-inorganic IL-POM hybrids

Because of the discrete framework of the POMs as mentioned in one of the sections, they can be tuned at molecular level. Amalgamation of the components of choices with POMs, will finally decide the physical properties of POM-based hybrid [87, 116-121]. Properties like solubility, charge, electrochemical properties etc. can be well tuned by the type of organic moiety attached to the polyoxometalate [122,123]. Subunits appended to the POMs, allows union of properties of both the units while designing target application-based hybrids [92,120,124]. In organic-inorganic IL-POM based hybrids, electrostatic interaction is the dominant one, however the counter cations are the key factor in contributing other interactions like hydrogen-bonding, ion-dipole, van der-Waals interactions etc. All these interactions due to the cationic counterpart is the fundamental reason of solubility and insolubility of the hybrids generated. Suitable IL cations when combined with POM, new application can be designed based on the synergistic effect of both the counter parts [125]. Thus, counter cations play an important role in deciding the final property of the hybrid. These ionic liquids based polyoxometalate hybrid salts generally display melting point higher than 200 ºC. Synthesis of such hybrids are performed by exchanging protons of the POM by the organic counter cation of the ionic liquid. There are many reports in which the anionic POM counterpart in the organic-inorganic IL-POM based hybrids is not presented as the active catalyst [126]. When the cationic counterpart is appended with an application based functional group then it becomes a TSIL-POM hybrids, as the active site is now present in the cationic IL part. Examples of some of the synthesized hybrids are presented here where the counter cation plays the key role in deciding the melting point as well as the physical state of ionic liquid based polyoxometalate hybrids. Tetraalkylphosphonium salt of Keggin anion yielded melting point of 200 ºC and the hybrid was obtained as solid salt whereas trihexyl(tetradecyl)phosphonium salt of the Keggin anion yielded a melting point of 60 ºC. However, the trihexyl(tetradecyl)phosphonium salt of the isopolytungstate anion yielded to be a room temperature ionic liquid. All the three hybrids were prepared under same reaction condition, but the combination of cations and anions made a huge difference in their chemical as well as physical properties. This work was done to explore the synthetic approach by different combinations of the organic cation and anion and examine the efficacy of hybrids as electroactive solvents [127]. Leng et al. synthesized sulfonic acid

functionalized quaternary alkyl ammonium-based POM hybrid where the cationic counterpart was the active site of the catalyst [128]. The catalyst was used for esterification reaction where the cation part of the hybrid was used for this acid catalysed reaction. In addition, because of the presence of both IL and POM subunits in the hybrid, the catalyst served as a phase transfer catalyst providing advantages of both homogeneous and heterogeneous catalysts. Same hybrid was used in combination with H_2O_2 as oxidant, where the anionic subunit acted as the active site for desulfurization reactions [128]. Thus, a numerous combination of task specific ionic liquid based polyoxometalate hybrids can be designed and their properties can be investigated.

1A.6 Importance of organic-inorganic IL-POM based hybrids as phase transfer oxidation catalyst

Homogeneous and heterogeneous catalysis are two basic catalytic technologies for production of target chemicals [92,129-137]. Although homogeneous catalysts show high activity compared to heterogeneous catalysts but laborious separation, recovery after completion of the reaction creates limitations in both the processes [135]. Researchers have already made innumerable efforts in developing a better catalysis technology with advantages of both homogeneous and heterogeneous catalysis. Phase transfer catalysis is a way in which catalysts changes phase and become homogeneous during the reaction while it separates from the reaction mixture after the reaction ends [128,136-148]. Thus, phase transfer catalysts (PTCs), can be easily recovered and reused [128,138-140]. A combination of high activity, proper accessibility of the reactants to catalytically active sites offered by homogeneous catalysts along with the facile separation and reuse provided by heterogeneous catalysts makes phase transfer catalyst favourable towards reaction sustainability. Combination of organic cations with the polyoxometalates are promising PTCs and various PTCs based on ionic liquids and polyoxometalates have been explored so far [137-148]. A brief information on few types of phase transfer catalyst is mentioned below:

i. **Reaction controlled phase transfer reaction**

Reaction controlled phase transfer catalysts are those catalysts that forms active catalytic compound and solubilise when encounters one of the reactants. The active compounds then react with the other reactants and produce the desired product. After the reactants are

used up during the reaction, the catalyst returns to its insoluble state and can be easily separated from the products [13].

ii. Temperature controlled phase transfer reaction

Temperature controlled phase transfer catalysts are those catalysts that changes phases upon variation of temperature. The catalysts become solvable at certain temperature and gets precipitated at certain temperature [13].

iii. Photo catalysed phase transfer reaction

Photo catalysed phase transfer catalysts are those that changes phase upon UV and visible light irradiation. This property of the catalyst allows the catalysts to be recycled through light responsive reversible phase transfer process [13].

1A.6.1 Literature review on organic-inorganic IL-POM based hybrid in oxidation reactions

Oxidation of alcohols to carbonyl compounds is an industrially important transformation reaction and researchers are finding cheaper and safer processes for this transformation [149]. Considering the importance of carbonyl compounds used as intermediates in several organic synthesis, the improvement in the oxidation processes comprises of a vital area of research both in academia and industrial [150, 151]. Reagents like chromates or permanganate apart from being expensive, they suffer from stoichiometric oxygen donor and are highly toxic in nature. Use of air or molecular oxygen in catalytic oxidation methods are a great alternative from the economic and environmental viewpoint [129,152-160]. However, requirement of high amount of catalyst in presence of acidic environment as well as low product yield serves as a major disadvantage while using these protocols [161,162]. Catalysis has always been the crucial technology for such chemical transformation. Developing environment-friendly processes are the new goal of researchers in chemistry. Phase transfer catalysis is a process which fulfils the necessity of sustainability in the catalysis process. Combination of advantages found in homogeneous and heterogeneous catalysis separately can be achieved in phase transfer catalysis. Designing phase transfer catalyst (PTCs), that suits the necessity of the reaction is an interesting topic of research. Phase transfer catalysts changes phases from heterogeneous to homogeneous during the reaction and becomes unsolvable or heterogeneous after the catalysis for easy recovery and reuse [128,137-140].

As it was already mentioned in the above sections that polyoxometalates for their unique acid/base and redox features are normally used as oxidation catalysts. Polyoxometalates are considered as a suitable candidate for designing phase transfer catalyst. The ability to incorporate counter cations into POM anions tunes molecular structures of the POM-anions. A good choice of counter-cation brings about change in physical and chemical property of the new hybrid including solubility thus constructing PTCs. Depending on the properties induced in the catalysts, they can be classified as reaction-controlled, temperature-responsive, and photo-sensitive phase transfer catalysts [13]. Modification of POMs with the ionic liquid cation by ion exchange also led to formation of some organic-inorganic IL-POM based hybrids with solvent selective behaviour for their solubility [128,137-140,163,164]. The structures of cation and anion in the constituent ion pair is responsible for the phase transfer process and the selection of suitable solvent for specific reactions is equally important step while performing the reaction [128,137-140,165,166].

Polyoxometalates as oxidative phase transfer catalyst is explored in various forms. A very active compound, Venturello anion ($\{PO_4[WO(O_2)_2]_4\}^{3-}$) is studied and used by many researchers. Zheng et al. in 2013, synthesized a Venturello anion polyoxometalate combined with surfactant-based cation. The compound $[C_{16}H_{33}(CH_3)_2NOH]_3\{PO_4[WO(O_2)_2]_4\}$ was then encapsulated in silica based nanochannels and used as micro reaction-controlled phase transfer catalytic system for oxidative desulfurization. Reaction was carried out at mild conditions at 70 °C with a molar ratio of 4:1 for H_2O_2/substrate with 100% S-conversion. It was observed that the performance of reaction was enhanced using this catalytic system. Hence, this catalytic system contributes a strategy towards production of sulphur free fuel system [167].

Hamamoto et al. synthesized a dye labelled catalytic system comprised of phosphotungstic acid and poly(*N*- isopropylacrylamide) polymer. The synthesised micellar aggregate was used for oxidation of alcohols in presence of H_2O_2 (**Scheme 1A.2**). The hydrophobic nature of poly(*N*- isopropylacrylamide) allowed the reaction to be performed at higher temperature of 90 °C and 0.1 mol% of catalyst yielded greater than 90% yield of products. Formation of a stable emulsion of the catalytic system at higher temperature elevated the catalytic performance in oxidation of alcohols. Furthermore, precipitation of the catalytic

system on cooling makes it a temperature responsive catalyst. The easy recyclability and reuse make it a very efficient catalytic system [137].
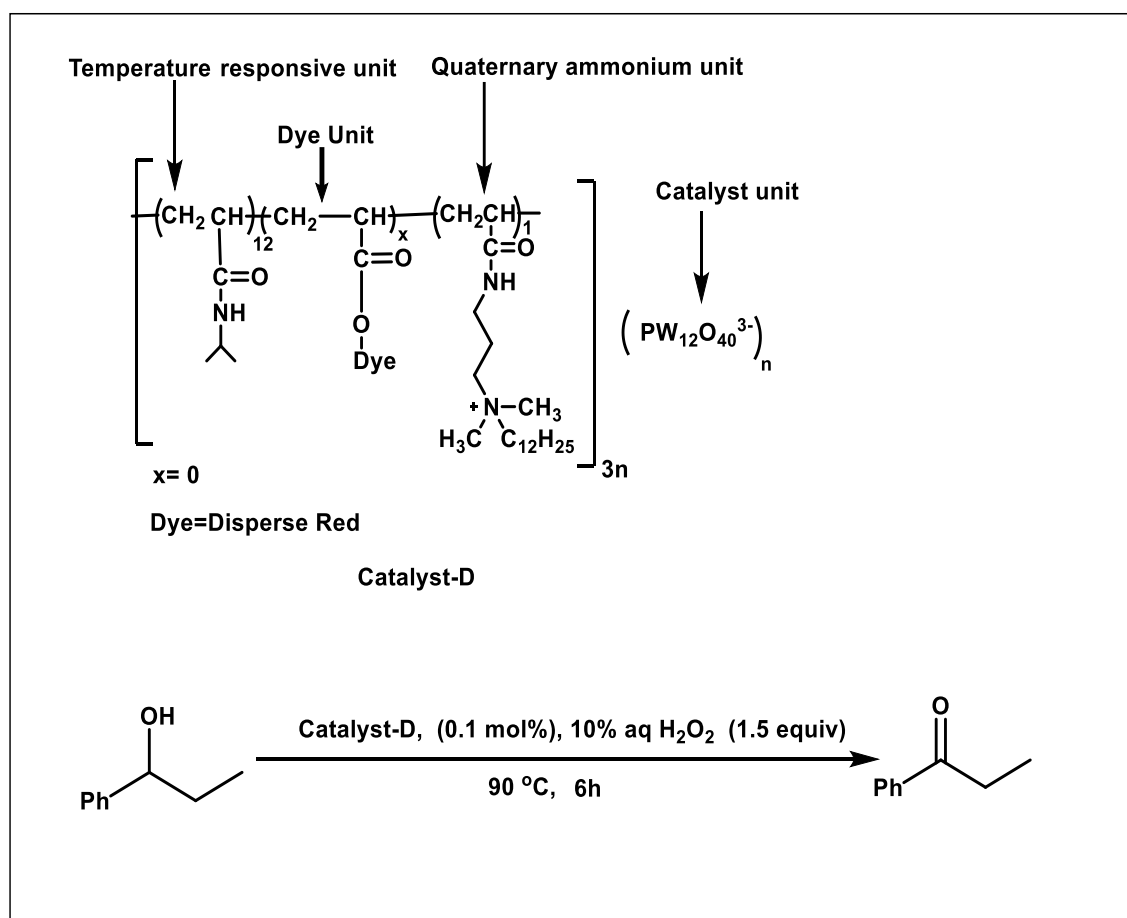
Scheme 1A.2 Application of thermomorphic polymer-supported $PW_{12}O_{40}{}^{3-}$ complex designed by Hamamoto et al. for oxidation of 1-phenyl-1-propanol catalyzed by **Catalyst D** [137]**.**

Yahya et al. synthesized amine terminated polyisobutylene oligomer-bounded Keggin polyoxometalates (PIB-POM) and are used as oxidation catalyst for both oxidative desulfurization and alkene epoxidation in presence of H_2O_2. The reaction was carried out in a biphasic heptane-water two phase system and reaction proceeded via peroxo-polyoxometalate intermediate. The product sulphone, being insoluble in water precipitated out as white powder which was quantitatively extracted using acetonitrile or dimethylformamide from the heptane water biphasic system. The PIB-POM catalytic system being insoluble in acetonitrile or dimethylformamide was easily recycled and recovered and used further for five more times without any loss in catalytic activity. With PIB/POM molar ratio (6:1), 100% dibenzothiophene conversion in 0.5 h at 60 ºC was observed with phosphotungstic acid as the polyoxometalate. The high activity of the

catalytic system was explained because of the higher phase transfer capability of the long hydrocarbon PIB surfactant comprising of a total of 70 carbon atoms. This system was observed to get >99% efficiency of H_2O_2, **Scheme 1A.3** [168].
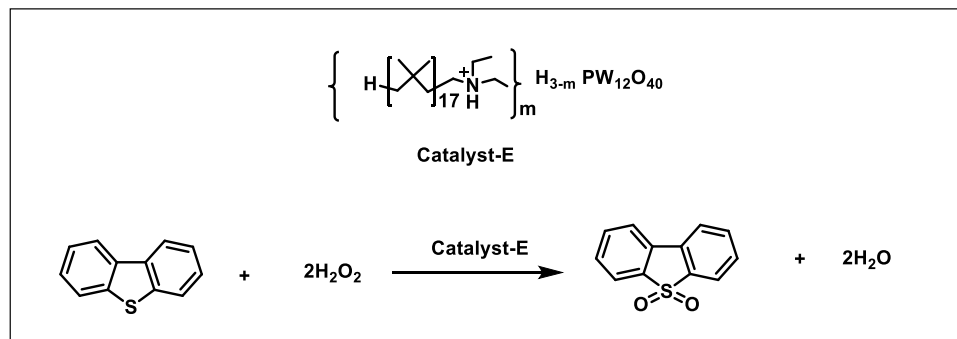

Scheme 1A.3: Application of diethylamine terminated PIB oligomer bound Keggin POM, (**Catalyst E**) for DBT oxidations, Yahya et al. [168].

Chen et al. incorporated phosphotungstic acid with dendritic polyamidoamine (PAMAM) and synthesized PAMAM dendrimer-hybridized phosphotungstate material (PW–PAMAM) by partial protonation of the amine groups in PAMAM. The material was used for selective oxidation of alcohols to correspond aldehydes at 100 ºC in presence of H_2O_2. The redox properties of the phosphotungstate anion were tuned by the positive dendrimer effect of the PAMAM counteraction. Incorporation of dendritic PAMAM into the HPW anions provided the resultant hybrid with a specific property of inverse dissolution–precipitation of the catalyst in water on addition of H_2O_2 and thus the catalyst behaves as a reaction-controlled phase transfer catalyst. These offered the reaction with significant enhancement in conversion. The catalyst turns out to be homogeneous with heterogeneous biphasic separation in water. Different generations of PW-PAMAM-Gn (n=1,2,3) are used. However, the PW–PAMAM-G1 showed gave conversion of 94% with 96% selectivity in 6 h for generation of benzaldehyde from benzyl alcohol [169].

Ming-Lin Guo and his team used hexadecyl trimethyl ammonium decatungstate catalyst in combination with hydrogen peroxide as oxidant for oxidation of alcohols. It was observed that the respective catalyst acted as a switchable homogeneous to heterogeneous catalyst. The catalyst becomes soluble on addition of reaction substrate and H_2O_2 and after complete decomposition of H_2O_2, the catalyst precipitates out from the reaction mixture. The reaction was carried out for 2 hours at 100 °C with cyclohexanone yield of 89.1% [165].

Ding et al. in 2011, used $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ and explored it for oxidation of alcohols and pyridines in presence of hydrogen peroxide. The catalyst acted as temperature-controlled phase transfer catalyst with excellent yield of N-oxides and ketones. The use of 1:5 molar ratios of benzyl alcohol / (30% aq.) H_2O_2 with 8 µmol catalyst in 2 mL of 1,4-dioxane at 85 °C has a conversion (mol%) of 99% benzaldehyde in 7 hours. Similar reaction condition with 1:5 molar ratios of pyridine /(30% aq.) H_2O_2 with 8 µmol catalyst using 2 mL of 1,4-dioxane at 65 °C yielded 99% of corresponding N-oxide. Here, the catalyst turned out to be a temperature-controlled phase transfer catalyst as it precipitates back from the reaction mixture on cooling which was effectively recycled for several catalytic cycles [170].

Zhou and his group synthesized three polyoxomolybdates $[Hmim]_4Mo_8O_{26}$ (Hmim = 1-hexyl-3-methylimidazolium), $[Dhmim]_4Mo_8O_{26}$ (Dhmim = 1,2-dimethyl-3-hexylimidazolium) and $[Hpy]_4Mo_8O_{26}\cdot H_2O$ (Hpy = 1-hexylpyridinium) as organic-inorganic hybrids, **Fig 1A.7**. The two hybrids $[Hmim]_4Mo_8O_{26}$ and $[Dhmim]_4Mo_8O_{26}$ had an epoxide yield of 100% after 1.5 hours of reaction in presence of 1.5 equiv. of H_2O_2 to substrate and CH_3CN as solvent at 70 ºC. However, the hybrid $[Hpy]_4Mo_8O_{26}\cdot H_2O$, yielded 93% of epoxide after 1.5 hours of reaction under the same reaction condition. Self-precipitating characteristic of all the three catalysts adds on an advantage towards reuse and recyclability. All the catalysts showed excellent efficiency with no loss in activity for 10 catalytic cycles [140].
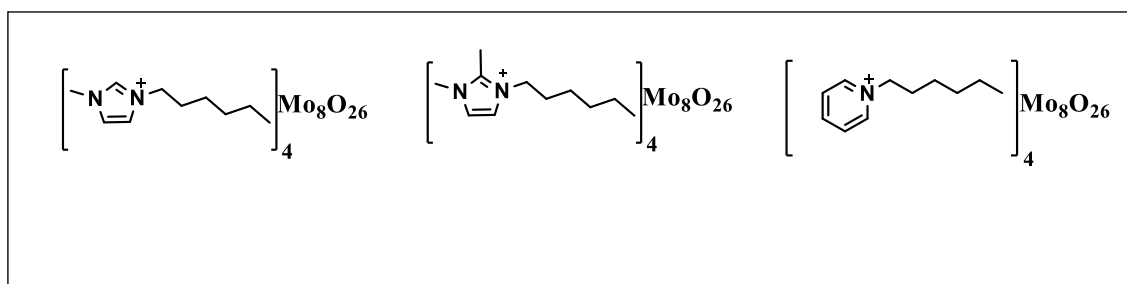
Fig. 1A.7: Structures of polyoxomolybdates synthesized by Zhou and his group [140].

In 2013, Yang and co-workers developed surfactant encapsulated polyoxometalate based complex (Azo-SEP) with structural formula $[[(AzoC_6)_2N]_9Na_3[Zn_5W_{19}O_{68}]$, **Fig.1A.8**. Azo group undergoes photoisomerization induced polarity change in presence light irradiation and this characteristic property of the complex was responsible for reversible phase transfer of the complex between toluene and H_2O/DMF (1:1 vol/vol) mixed solution.

The complex showed excellent homogeneous catalytic activity and heterogeneous separation in oxidation of sulfides to sulfones [139].
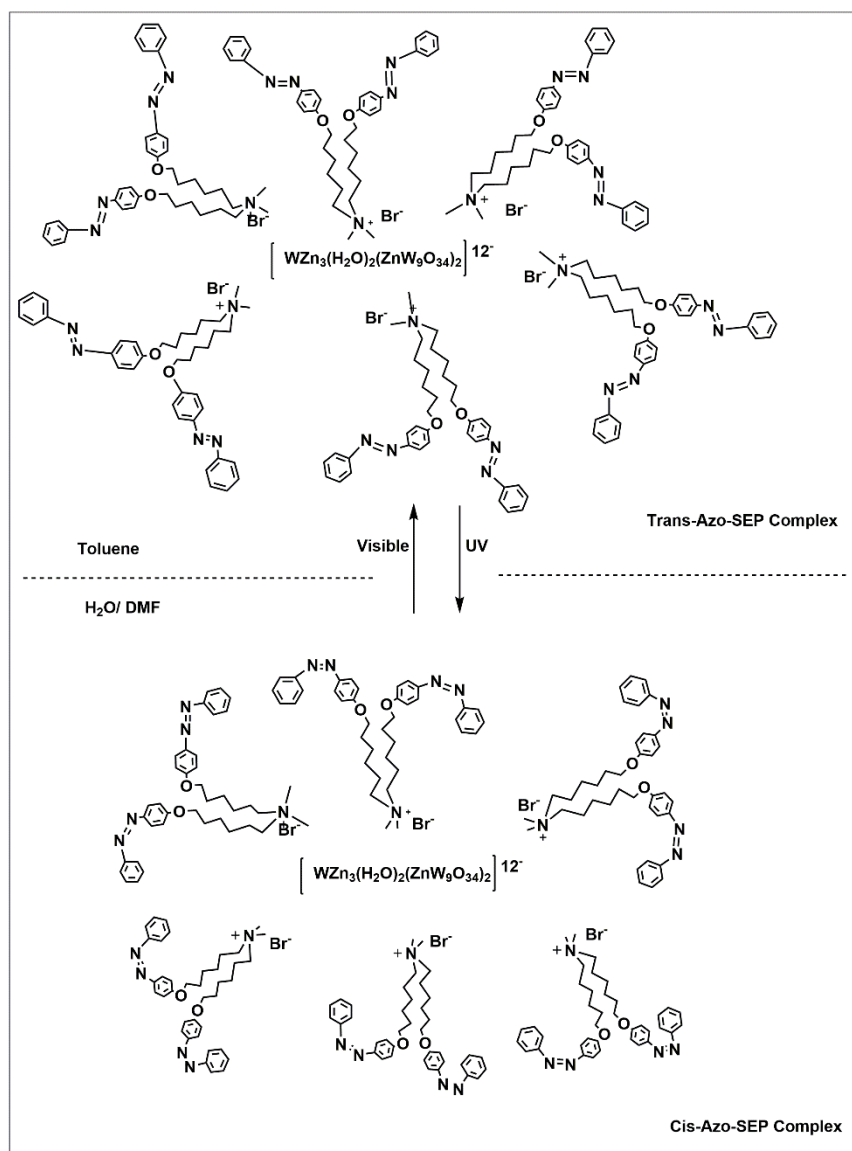
Fig.1A.8: A photo-responsive surfactant encapsulated polyoxometalate based complex (Azo-SEP) developed by Wu and co-workers [139].

1A.7 Importance of degradation of organic pollutant and role of polyoxometalates

A noticeable rise in manufacture and synthesis of various toxic organic chemicals like herbicides, pesticides, plastics etc. are seen to trigger a lot of human health, wildlife, environmental toxicity issues [171]. Their persistence and bioaccumulation extent has increased the intensity of toxicity to a greater magnitude [172]. Aquatic ecosystems are

mostly affected by the organic pollutants. The aquatic water bodies are mainly polluted by industrial effluents, municipal as well as domestic sewage and also by agricultural waste. Risky and high concentrations of pesticides and herbicides used in farming and agricultural interest have potential to cause chronic diseases [173]. These toxic organic chemicals have the capacity to cause disorder in endocrine, nervous, reproductive, immune system [174]. Carbon based organic pollutants and their eco-toxicological effects on environment has been a topic of concern. For this cause, it is necessary to evaluate and develop degradation systems which converts all these toxic organic pollutants into harmless products [171]. Advanced oxidation process (AOP) is one of the most promising technologies that uses the highly reactive hydroxyl radicals for wastewater treatments. heterogeneous catalysts are practically more advantageous than homogeneous catalyst from the point of view of their reuse and recyclability. Numerous efforts on synthesis and use of economically viable metal-based Fenton AOPs are done for generation of OH• from hydrogen peroxide. Many metallic species can decompose H_2O_2 to OH• and are experimentally examined for oxidation of organic pollutants [175]. Polyoxometalates (POMs) are utilised a lot for oxidation of organic pollutants in presence of H_2O_2 [176]. The versatility in structure as well as composition of these oxyanions allows designing and synthesis of tailor-made POMs catalysts [177]. POMs are observed to have high catalytic decomposition capacity of H_2O_2.These oxyanions have been widely used in oxidative degradation of organic pollutants using H_2O_2 as oxidants [175,178]. The diversity in this group of oxyanions have made them structured and efficient tailor-made catalyst for oxidative degradation of organic pollutants.

1A.7.1 Literature review on organic-inorganic IL-POM based hybrids used in oxidative degradation of pesticides

Gould et al. performed a comparative study in which ten different polyoxotungstate and polyoxomolybdate complexes with a variety of stereochemistry are found to display stronger catalytic activity than $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ respectively. These complexes were used as catalysts in presence of benign oxidant H_2O_2 and kinetic study for bleaching of methyl orange and crocetin in aqueous medium was reported [178].

In 2005, Lei et al. synthesized a hybrid composed of resin and $PW_{12}O_{40}^{3-}$ via electrostatic interaction. The POM/ resin material was then utilised for degradation of rhodamine B (RB) dye using H_2O_2 as oxidant. The degradation reaction was carried out under visible

light. The degradation and mineralization mechanism of the dye was proposed to be proceeded via generation of an active peroxo-intermediate after the interaction of the POM/resin material with H_2O_2. The synthesized POM/ resin catalyst in combination with H_2O_2 achieved total organic carbon removal of 22%. The heterogeneous catalyst was observed to show excellent stability and reusability [179].

In 2016, Zhia et al. prepared a hybrid with silicotungstic acid (SiW) incorporated with ferric chloride (Fe III), lysine (Lys). The material (Fe^{III}LysSiW) with formula [Fe(H_2O)_5(C_6H_{14}N_2O_2)]HSiW_{12}O_{40}·8H_2O$ was used as heterogeneous catalyst for degradation of 4-chlorophenol in presence of H_2O_2. The reaction was done in both dark and under visible light. The use of 1 g/L of catalyst degraded 100mg/L solution of 4-chlorophenol in presence of 20 mmol/L of H_2O_2 in 40 minutes in dark and in 15 mins under visible light respectively. 71.3% of TOC removal was obtained in dark and was 98% under visible light when the reaction was continued for 3 hours of reaction time. The degradation of 4- chlorophenol occurred via Fenton like oxidation process [180].

Yanjun Gong et al. reported a hybrid material composed of surface active ionic liquid (SAIL), i.e. N-decyl-N′- carboxymethyl imidazolium bromide ([*N*-C10, *N*′-COOH-Im]Br) with phosphotungstic acid (($H_3PW_{12}O_{40}$).The POM/[N-C10, N′-COOH-Im]Br hybrid material disassemble and assemble in response to pH variation. The hybrid material is explored as a degradation catalyst of methyl orange (MO) in presence of H_2O_2 in dark. The pH responsive assembly and disassembly of the hybrid material demonstrated in this report to address to catalyst poisoning complication [115].

1A.8. Importance of 3-substituted indole heterocyclic compounds

Multicomponent reactions are important synthetic strategy for synthesis of various heterocyclic compounds due to many advantages like simplicity in synthesis, low-cost efficiency along with greener approach towards reduction of chemical waste [181-185]. Multi component reactions involves at least three or more substrates in synthesis of major amount of targeted organic heterocyclic molecule. Heterocyclic compounds contain one or more heteroatoms (N, O, S, P) in the carbon containing cyclic compounds [186]. Many pharmaceutical preparations comprise of heterocyclic compounds as key structural unit [187]. Progress in development of synthetic methodologies for generation of wide variety of heterocyclic compounds with numerous pharmacological activities have become a powerful area of research. One of the important heterocycles which is crucial in synthesis

of drug molecule is the indole nucleus [188]. The 3-substituted indole nucleus with carbon substituents are significant in preparation of antipsychotic drugs [189]. Indole being a fundamental nucleus are reported to have numerous pharmacological properties like antibacterial [190], anti-inflammatory [191-193], cardiovascular [194], anticonvulsant [195] etc. In addition, 3-substitued indole moieties are reported to exhibit anti-inflammatory properties [196].   Indomethacin and tenidap, [**Fig.1A.9**] are two 3-substituted indole derivatives, used as non-steroidal anti-inflammatory drugs [197, 198]. These drugs are used for treatment of osteoarthritis and rheumatoid arthritis [199, 200]. **Fig. 1A.9** presents various compounds of 3-substituted indole derivatives with pharmacological properties [201].
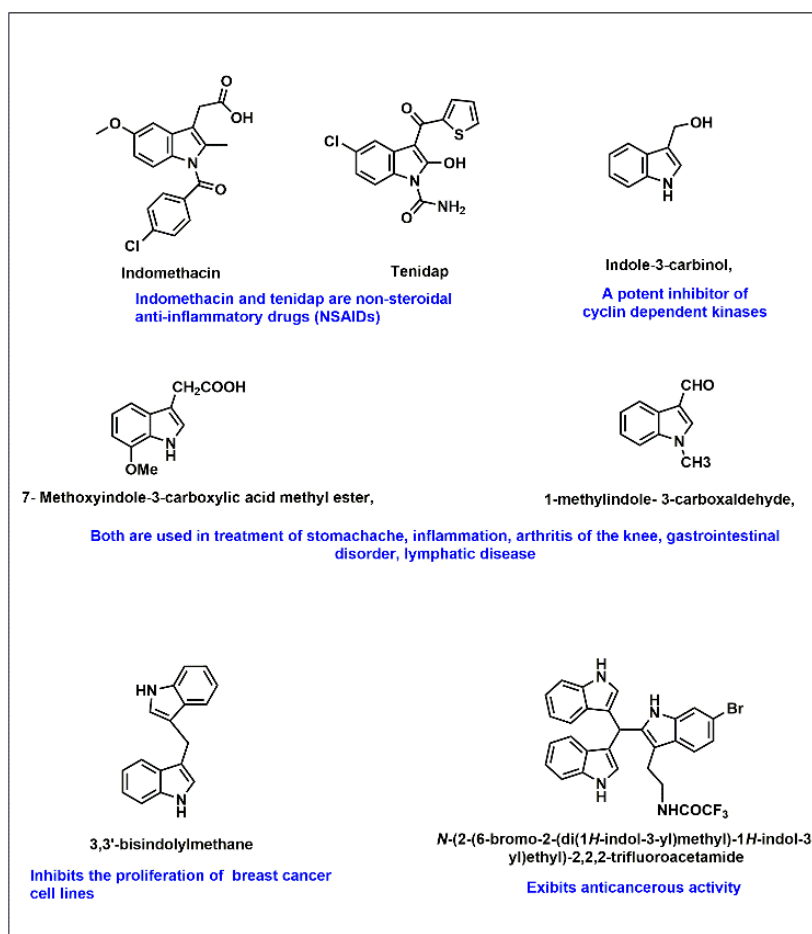

Fig. 1A.9 Structures of few 3-substituted indole derivatives with pharmacological properties.

Observing this important pharmacological importance of the 3-substituted indole compounds various multicomponent reaction synthetic approaches has been studied by researchers in view of drug discovery studies. Considering all the above reasons, we

synthesized few 3-substituted indole derivatives with Brönsted acid functionalized ionic liquid based polyoxometalate as acid catalyst.

Many groups of scientists have attempted various synthetic procedures and used different catalysts for generation of 3 -substituted indole derivatives. There is literature on use of polyoxometalates by different scientists for the same. Srihari et al. conducted the one pot coupling reaction reacting aldehyde, N-methylaniline and indole for synthesis of 3-substituted indoles using PMA-SiO$_2$. It was observed that presence of SiO$_2$ along with PMA (phosphomolybdic acid), resulted a single desired product. Similarly, the use of PMA alone also formed 3- substituted indole with a yield of 80% along with formation of bisindolylmethane as byproduct. At the same time, the desired product formed with 70 % yield without any byproduct during 36 hours in presence of SiO$_2$ only. The obtained results proved that union of PMA and SiO$_2$ together served as perfect catalyst for synthesis of 3-substituted indole as the desired product in majority, **Scheme 1A.4** [202].
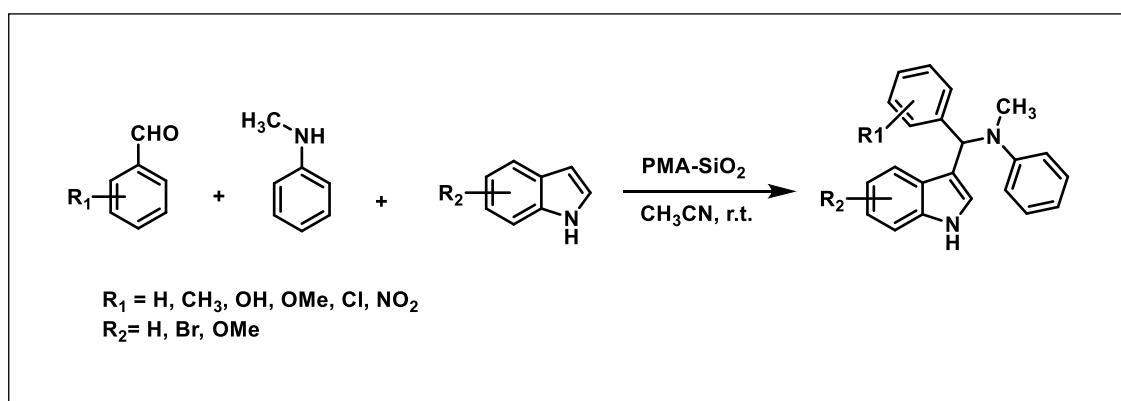
Scheme 1A.4: PMA-SiO$_2$ catalysed synthesis of 3-substituted indole [202].

Another example from literature on synthesis of the 3-substituted indoles using acidic ionic liquid was performed by Das et al. The reaction proceeded via generation of chalcones and then addition of indole resulted in 3-substituted indoles with excellent yields. The reaction was carried out in solvent free condition. The acidic ionic liquids 2-methyl-1, 3-disulfoimidazolium trifluoroacetate [MDSIM][CF$_3$COO] and 2- ethyl-1,3-disulfoimidazolium trifluoroacetate [EDSIM][CF$_3$COO] proved as efficient liquid catalyst for the desired product synthesis [203]. However, liquid acidic catalyst containing -SO$_3$H acidic groups can be in some measure corrosive in nature and their use in industry is hard. Numerous approaches have been made to overcome such limitations of acidic liquid catalyst to increase structural and thermal stability and designing ionic liquid modified heterogeneous catalysts is one of the ways. Our current work is focused on generating a

library of 3-substituted indoles involving selective formation of the chalcones as precursor for the conjugate addition of indole in one pot method using Brönsted acid functionalized ionic liquid and polyoxometalate modified heterogeneous catalyst for simple work up of reaction mixture to isolate the product as well as separation and recycling of the catalyst.

1A.8.1 Literature review on organic-inorganic IL-POM based hybrids used as acid catalysts

The use of conventional homogeneous acid catalyst is corrosive and laborious to recover from the reaction media. Synthesis of heterogeneous catalyst makes the catalyst recovery and reuse an easy task which is one of major advantages in catalytic reaction study. However partial dissolution and leaching are some of the major concerns while immobilization of acidic groups over various matrices [204]. The ability to incorporate active sites on the organic-inorganic IL-POM based hybrids by functionalization of cation or anion or both provides added advantages [128,138,140,205]. The organic-inorganic IL-POM based hybrids with acid functionalized counter cation from acidic ILs are utilised in acid catalysed reactions like esterification, transesterification and many more [13,128]. In this context, the organic-inorganic IL-POM based hybrids preparation techniques and stability somewhat addresses the concerned issues.

Leng et al. combined organic cation with heteropolyacid and explored their catalytic activities in esterification reactions. The three propane sulfonates functionalized polyoxometalate hybrids [MIMPS]$_3$PW$_{12}$O$_{40}$, [PyPS]$_3$PW$_{12}$O$_{40}$ and [TEAPS]$_3$PW$_{12}$O$_{40}$ were used as reaction-induced self-separation catalysts for esterification of polycarboxylic acids **(Scheme 1A.5)**. The selective solubility of the substrates and products along with high melting point of the organic-inorganic IL-POM based hybrids results in switch ability from homogeneous to heterogeneous catalysis making their recovery and reuse simple [128]. Using the same organic-inorganic IL-POM based hybrids catalysts, the esterification of monocarboxylic acid is performed as temperature-controlled liquid-liquid biphasic reaction media catalysts and also as heterogeneous catalysts (**Scheme 1A.5)** [206]. In 2009, Zhang et al. synthesized pseudo liquid organic salt of phosphotungstic anion with SO$_3$H-functionalized triphenylphosphonium, [TPSPP]$_3$PW$_{12}$O$_{40}$ where the polar substrates penetrate in bulk of the POMs, increasing easy mass transfer and substrate accessibility to the active catalytic sites. Thereby, the existence of heteropolyanion stabilizes the generated carbonium intermediates with increasing efficiency of the reaction.

The catalytic system was observed to display high product yield of 90-97% with various substrates. In addition, the catalyst was easily recovered and reused up to 10 catalytic cycles with little reduction in yield [207].
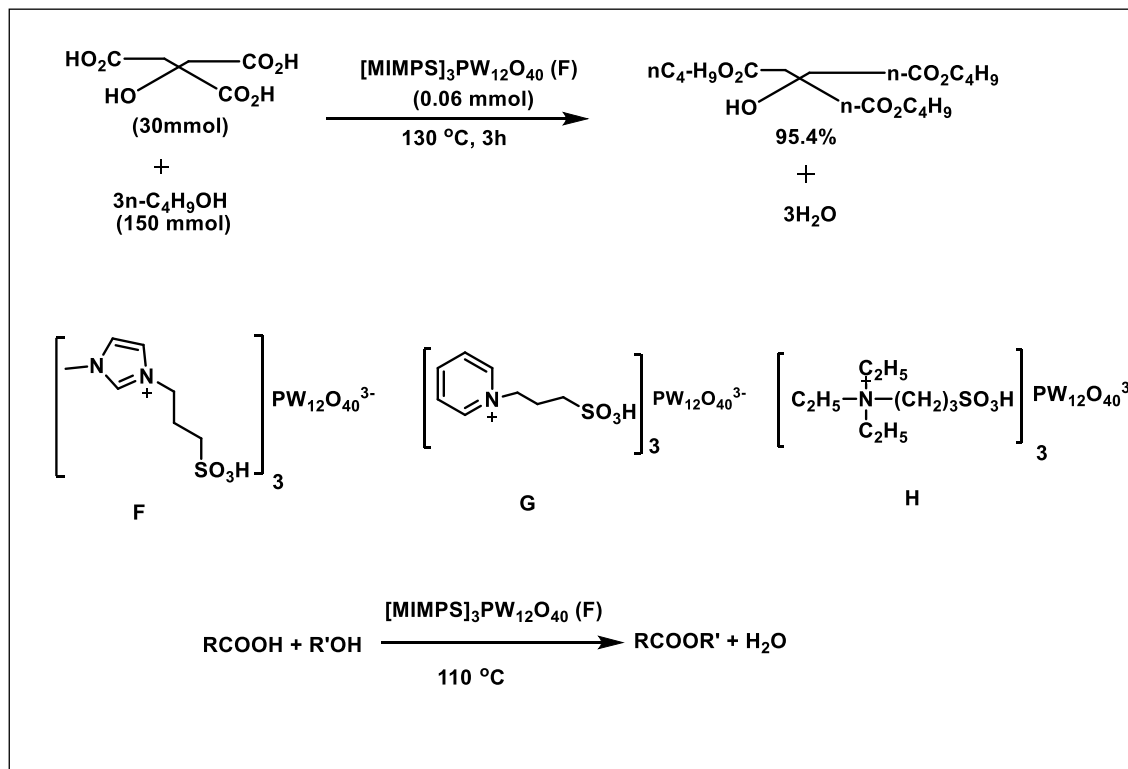
Scheme 1A.5: -SO_3H functionalized polyoxometalate hybrids reported by Leng et al. and used for acid catalyzed reaction.

Ghasemi and his group in 2016, reported synthesis of system consisting supported IL bounded to diatomaceous earth (DE) for immobilization of phosphotungstate and bisulphate anion. The bisulphate anion catalyst acted as heterogeneous Brönsted acid catalyst and its catalytic effect was explored on aza-Michael-type addition, **Scheme 1A.6**. The dual catalytic effect of anionic polyoxometalates as Brønsted and Lewis acids along with intermediates being stabilized by polyoxometalate anion showed better results than the bisulphate anion catalyst. Being heterogeneous, the polyoxometalate based catalytic system showed 80-95% yield with various substrates. The catalytic system is easily recoverable from reaction media [208].
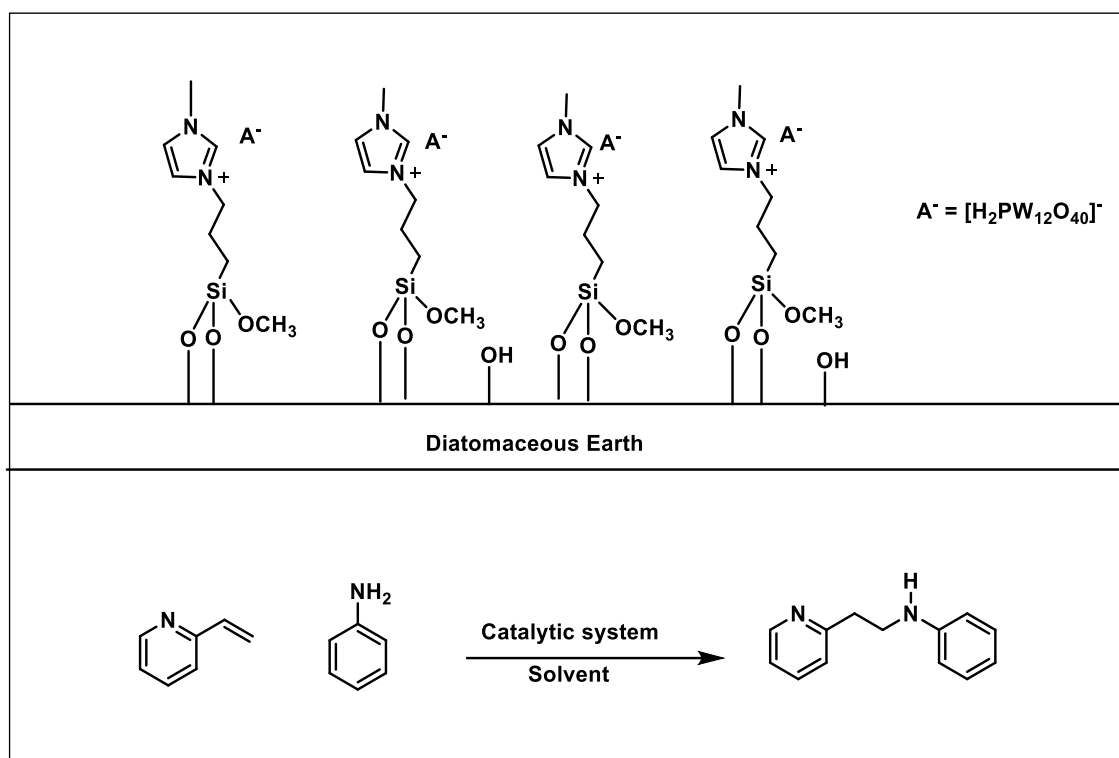
Scheme 1A.6: Anion-exchanged supported IL covalently bounded on the DE surfaces used as catalyst for aza-Michael reaction [208].

1A.9 Importance of metal extraction and role of ionic liquids in the same

The increase of heavy metal flux into the water bodies is creating concern as these heavy metals persists over time and are dangerous and highly toxic to the environment [209]. Several technologies like precipitation, solvent extraction, ion exchange, etc has been long established and used [210]. Solvent extraction is the most widely used technology for separation of metals from aqueous medium. Traditionally, various extraction agents like di(2-ethylhexyl) phosphoric acid, tris(2-ethylhexyl)amine, liquid phosphine oxides, etc are used in combination with organic solvent for the extraction purpose [211,212]. However, organic solvent being volatile in nature gets lost which is not a preferable property for a diluent to be used for solvent extraction. Here comes the use of ionic liquid which has advantages like low vapour pressure which reduces the risk of environmental damage caused by volatile organic solvents [213,214]. For biphasic metal extraction, the hydrophobicity, solubility, viscosity etc needs to be tuned in designing ionic liquids and this can be done by altering the substituent group, functionality attached to the organic cation or anion [214-216].

Green processes are a major need towards hydrometallurgy. Functionalized ionic liquid itself can act as complexing agent along with transport matrix without extra addition of extracting agents [217,218]. The use of ionic liquid as transport matrix turns down the use of volatile organic solvent during the extraction process [219].

1A.9.1 Literature on ionic liquids used as solvent for metal extraction

Metal extraction, their recyclability and uses are increasing globally and researchers are developing new technologies for meeting such demands. Ionic liquids and their physico-chemical properties play an important role in metal extraction process and their ionic character leads to many possible metal transfer mechanisms which was not possible using molecular liquids as extraction solvent. Therefore, ionic liquids are considered as relevant alternatives to molecular solvents in case of metal extraction. Biphasic metal extraction from aqueous medium using ionic liquid generally uses ion exchange mechanism. Hence the metal transfer process causes degradation of ionic liquid into the aqueous medium polluting the same. Aqueous medium contamination can be suppressed by designing ionic liquids with few structural changes that controls the metal extraction mechanistic pathway. Different factors like chemical structure of ionic liquid, hydrophobicity of the ionic liquid etc. make a large influence in controlling the metal extraction mechanism and efficiency which have very less impact while organic liquids are used instead. Researchers are now designing ILs promoting IL-aqueous biphasic extraction systems based on a mechanism that would limit the above-mentioned disadvantages and advance extraction efficiency. One of the limitations mentioned above is partitioning of the extraction agents into the aqueous medium contaminating it and lowering the extraction efficiency. Building in metal coordinating groups into the constituent ions of the ILs, restrict the movement of extractant thus limiting the contamination [220]. Anions like salicylate, thiosalicylate, benzoate, methionate, β-diketonate etc. can be termed as task specific ionic liquid as these are strong metal coordinating agents [218,221-228]. Another strategy of extraction of metal ions from aqueous phase to IL phase is utilization of ionizable ligands as extractants. For example, Reyna-González et al. synthesized [3-BuPyr][NTf$_2$], 3-butylpyridinium bis(trifluoromethanesulfonyl)imide, and utilized it for Cu(II) metal ion extraction from aqueous medium. The extraction process involves deprotonation of the hydrogen atom forming H$_3$O$^+$ and transfers into the aqueous phase in exchange of Cu (II) ions into the IL phase and thus interacts with the IL. The IL phase consisting of the Cu-IL complex was

analysed using different analytical techniques like cyclic voltammetry (CV), UV–vis as well as NMR spectroscopies. Electrodeposition of copper from IL phase was also performed on Pt electrodes. Treatment of IL phase containing Cu-IL complex with HCl lead to back-stripping of Cu from the IL and thus IL was recovered and reused for further extraction, (**Fig. 1A.10a**) [229].

Guillon et al. prepared ILs with ester derivative of glycine betaine as cationic counterpart and anionic counterpart consisting of bis(trifluoromethylsulfonyl)imide (Tf$_2$N) or dicyanamide (Dca) for extraction of Cu(II) ions from aqueous medium. They illustrated that designing simple ionic liquids with ions like dicyanamide have potential in extraction of metal ions from aqueous medium. It was observed that the extraction mechanism proceeded via cation exchange as well as ion-pairing. Various spectroscopic techniques like UV-Vis, XAS was performed for analysis of Cu-IL coordination (**Fig. 1A.10b**) [230].

(a)

3-butylpyridin-1-ium bis((trifluoromethyl)sulfonyl)imide

(b)

tributyl(2-ethoxy-2-oxoethyl)ammonium based ionic liquids
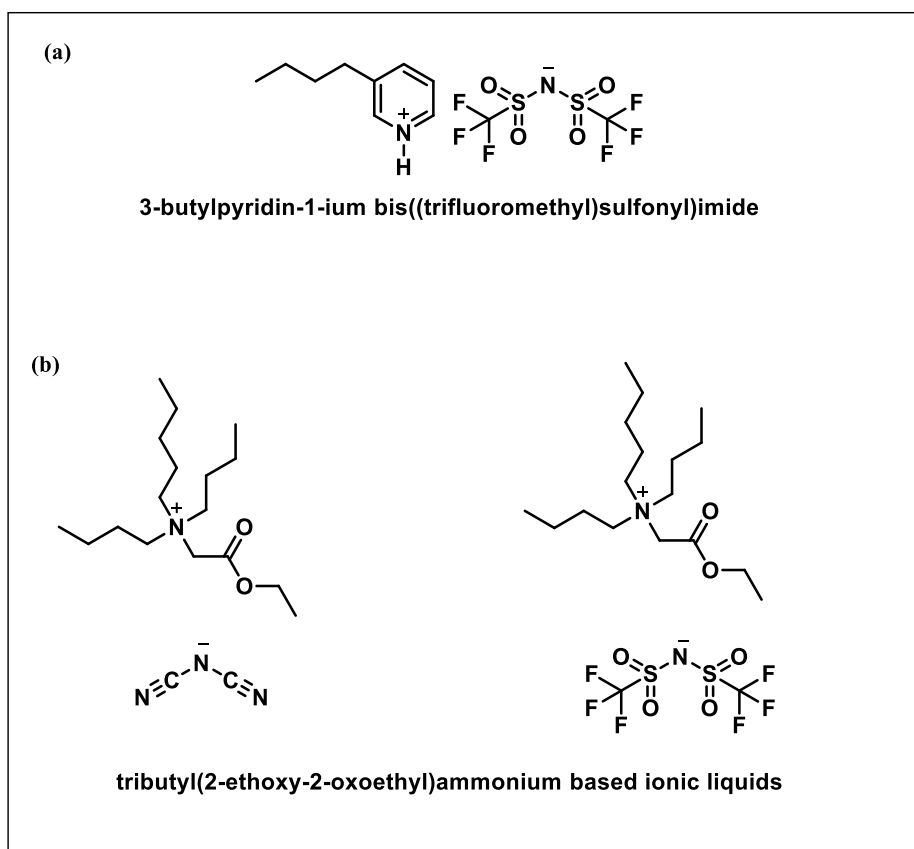
Fig. 1A.10: Structures of ILs prepared by Reyna-González et al. [229] and Guillon et al. [230].

Preethi et al. used 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF$_6$] as a biphasic medium for extraction of Zn from aqueous medium. The extraction was done using three different methods of Dispersive Liquid-Liquid Microextraction (DLLME),

using conventional DLLME, temperature-controlled DLLME and ultrasound-assisted DLLME methods. The ultrasound assisted DLLME method proved to be the most effective method for Zn extraction and this method was used for electroplating industrial effluents with extraction recovery percentage of 87.4%. Stripping of ionic liquid was also possible using sulphuric acid and was reused for several times [231]. Similar extraction of rare earth metals Sm(III) and La(III) was done over Co(II) and Ni(II). This extraction was done using symmetrical dihexyl imidazolium nitrate ionic liquid as solvent [232]. Another task specific ionic liquids with aminodiacetic acid moieties as di-tert-butyl esters is used as metal chelators for metals Cu(II), Ni(II) and Co(II) in aqueous solutions. The complexes are hydrophobic in nature due to presence of alkyl chains onto the imidazolium cation**, Scheme 1A.7** [233]. Homogeneous liquid-liquid extraction (HLLE) is another method in which the two liquids form homogeneous phase on change in temperature. This method is a very efficient one in liquid-liquid extraction. Depuydt et al. in 2015, employed an ionic liquid with a combination of ether-functionalised cation and bis(2-ethylhexyl)phosphate anion which is a thermomorphic ionic liquid with a lower critical solution temperature and this ionic liquid is used for extraction of first period of (3d) transition metals , **Fig. 1A.11** [234]. Onghena and Binnemans investigated on Sc recovery from red mud leachates and also from a multielement rare-earth metal solution. A comparison study was done between homogeneous liquid−liquid extraction (HLLE) processes and conventional liquid−liquid extraction using betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf$_2$N] (**Fig. 1A.12a**). The extraction mechanism proposed was based on slope analysis and extracted with stoichiometry of 1:3. Deprotonated betaine cation forms zwitterion and scandium is extracted as zwitterionic complex. The ionic liquid could be back extracted using HCl and precipitation by oxalic acid [235]. A very important exchange mechanism using nonfluorinated carboxyl-functionalized phosphonium IL [P$_{444}$C$_1$COOH]Cl and 16 wt % NaCl solution comprises of aqueous biphasic solution is proposed by Depuydt et al. (**Fig. 1A.12b**). In this mechanism, the deprotonated cation of the carboxyl functionalized ionic liquid forms zwitterion which is proposed for coordination of scandium (III) ions via the carboxylate ion. Extraction percentages of Sc(III) based on pH and contact time were investigated [236].
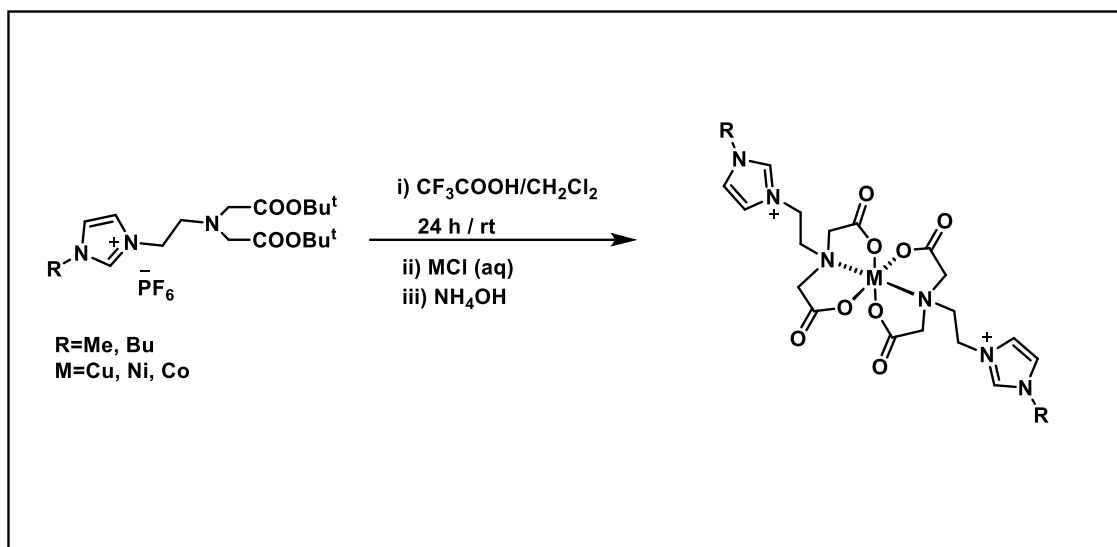
Scheme 1A.7: Formation of metal complexes using task specific ionic liquids with aminodiacetic acid moieties [233].
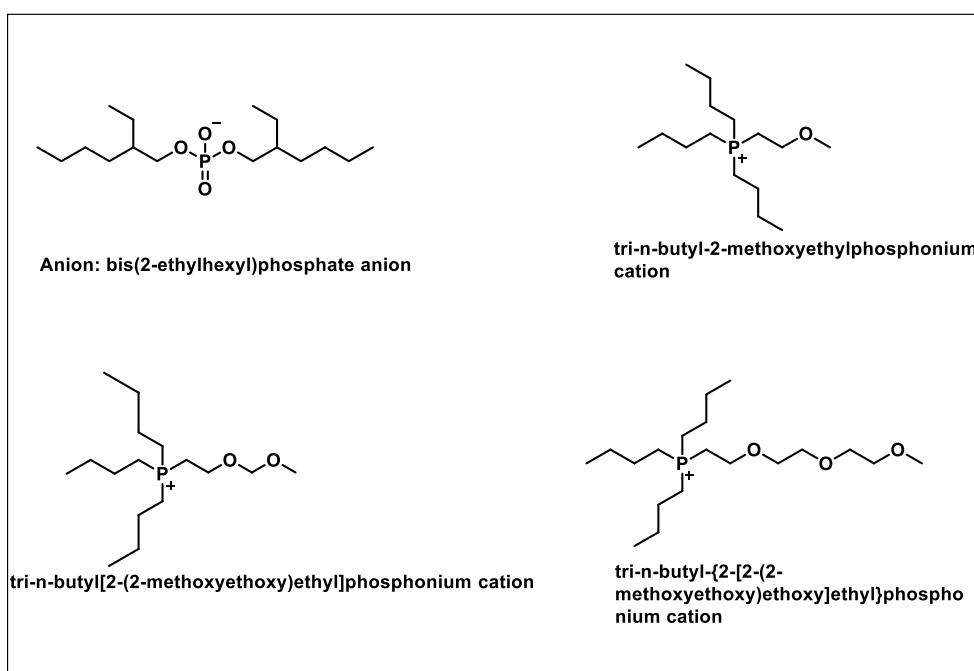
Fig. 1A.11: Structures of ILs used in metal extraction by Depuydt et al. [234].
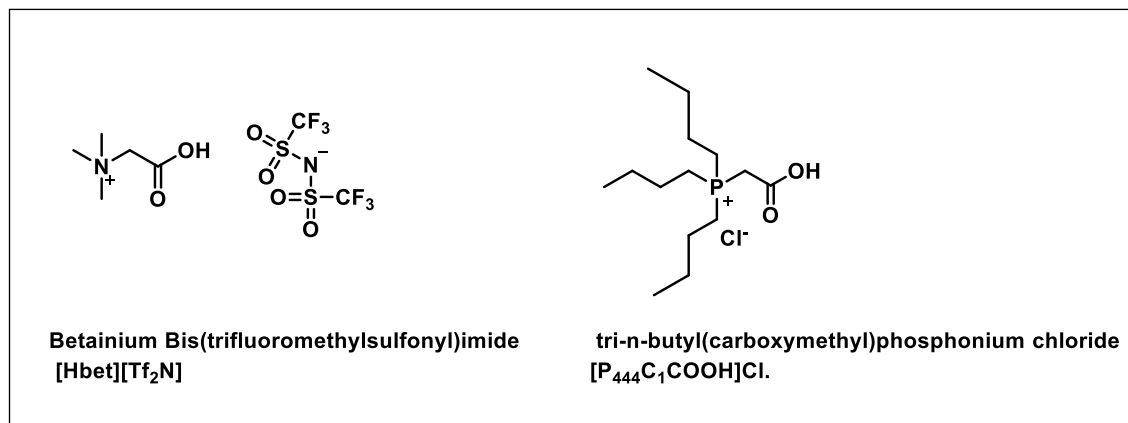
Fig. 1A.12: Chemical structures of (**a**) [Hbet][Tf₂N] and (**b**) [P₄₄₄C₁COOH] Cl.

Two carboxylic acid functionalized ionic liquid with property of upper critical solution temperature N-carboxymethylpyridinium bis- (trifluoromethylsulfonyl)imide ([HbetPy][Tf₂N]) and N-carboxymethyl-N-methylmorpholinium bis(trifluoromethylsulfonyl)imide ([HbetMor][Tf₂N]), (**Fig. 1A.13**) are prepared by Ding et al. These were explored towards extraction of Sc(III) in nitrate medium from mixture of five other rare earth metals including La, Nd, Eu, Ho, and Yb. Extraction mechanism occured via proton exchange mechanism evidenced from slope analysis as well as Fourier-transform infrared results [237].
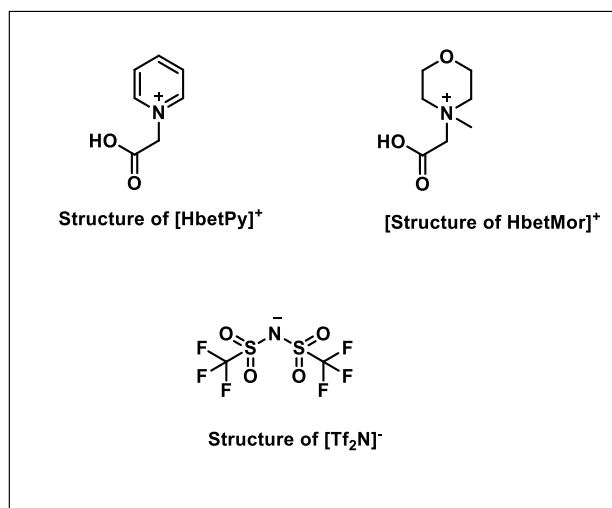
Fig. 1A.13: Structures of two carboxylic acid functionalized ionic liquids reported by Ding et al. [237].

1A.10 The objective of the present work

It has been reported that volatile solvent use in pharmaceutical production and post treatments leads to solvent wastages that are responsible for greenhouse emissions along with ground water pollution [238-245]. Here comes the role of ILs that are used in replacement to volatile organic solvents. Their non-flammability and non-volatility enhance the chemical synthesis conditions and proved to be an efficient substitute keeping in line with the principles of green chemistry. Tunability in the properties of the resultant ionic liquid by suitable selection of anions and cations has made them a very interesting field of research to work on. Besides that, different functional groups can also be incorporated into ionic liquids aiming to impart properties specific for application and these are called task specific ionic liquids (TSILs) [12]. Numerous TSILS are designed based on the prerequisite to applications like metal extraction [246], catalysis [247], organic synthesis [248] etc.

Regardless of all the advantages of ILs as catalysts, solvent, extractants etc., some of the -SO_3H or -COOH functionalized Brönsted acidic ILs are highly hygroscopic, and their highly viscous nature make their usage inconvenient for industrial scale although these acts as excellent catalyst in acid catalysed reactions performed in lab scale [249,250]. Here comes the need of generation of systems in which one can take the advantage of such functionalized ionic liquids but in solid form which become more manageable to handle even in industrial scale. The most efficient route to generate such systems is synthesis of organic-inorganic hybrids based on ionic liquid. The inorganic counterpart used for preparation of ionic liquid-based hybrids for this work is POMs. In these hybrids, the use of POMs as anionic counterpart with the organic counter cation of IL may generate different types of phase transfer catalyst giving advantages of both homogeneous and heterogeneous catalysis. As a reactive functional inorganic material, POMs undergo multi-electron redox cycles with outstanding structural stability and their high activity with low toxicity is a great advantage for using them in catalytic applications. But their hydrophilic nature proves to be most obvious drawback in its recyclability although they show excellent catalytic activity. By incorporating the POMs with ionic liquid solves the individual limitations of ILs as well as POMs. From this point of view, the development of organic-inorganic hybrids of IL cation tethered with functional groups and dynamic molecular structures are the best candidate for constructing ionic liquid based

polyoxometalate catalyst which can be used in task-oriented applications like oxidation, acid catalysis etc. The literature review of organic-inorganic IL-POM based hybrids reveals that vast number of POM based organic-inorganic hybrids have been isolated and used for many catalytic reactions [115,139,140,165,168-170,178-180]. Introduction of the ionic liquid counter cation into the POM modify their porosity as well as polarity of the POM scaffold. The resultant water tolerant organic-inorganic IL-POM based hybrids serve as both potential phase transfer catalyst as well as heterogeneous catalyst depending on versatility in the ionic liquid's molecular structures. Since, POMs are oxygen-enriched framework so, it was planned to synthesize -NSO$_3$H functionalized organic-inorganic IL-POM based hybrids as organic-inorganic hybrids for potential use as phase transfer oxidation catalysts for oxidation of alcohols in CH$_3$CN in presence of oxidant, heterogeneous oxidative degradation catalyst for water soluble herbicide metobromuron in H$_2$O as well as heterogeneous acid catalyst for preparation of 3-substituted indoles under environmentally benign conditions.

To fulfil the catalytic activities of organic-inorganic IL-POM based hybrids for these different types of reactions, it was aimed to design the cationic counter part by functionalizing as well as alkylating them according to the need of applications to perform. Moreover, the selection of type of cation in hybrid preparation for example ammonium or imidazolium may play an important role in the resultant characteristics of synthesized ionic liquid-polyoxometalate hybrids. This proposed work was planned to synthesize such hybrids and utilize them as catalysts in the above-mentioned reactions after characterization of the hybrids using various analytical techniques like ^{1}H NMR, ^{13}C NMR, FT-IR, elemental analysis, TGA, Raman, UV-Vis, SEM-EDX, ICP-OES, Powder-XRD etc.

Since one of the proposed objectives in this thesis work is metal extraction from aqueous phase by task specific ionic liquids (TSILs). For the metal ion extraction from aqueous phase, ionic liquids constituting weakly coordinating ions along with addition of extra extractants are needed. Yet, it should be noted that both ionic liquid and extractant should not contaminate the aqueous phase in the process. Therefore, it is very necessary to design ILs with certain specifications so that it fulfils all the requirements facilitating extraction process with minimum limitations. Designing the ILs with cation or anion comprising of metal coordinating moieties limits the possibility of loss of extractant into the aqueous

phase. Synthesis of such TSILs serves them to act as dual solvent as well as extractant itself [220]. A well-designed IL system can have functionalization in both cation or anion, however most of the synthesized TSILs have their cation functionalized. The cause behind this is the simple synthesis in quaternization of tertiary amine or phosphine or N-heterocycle with functionalized alkyl halide. There are also many examples of ILs with anions containing the metal-coordinating moieties. Few examples of anions are dicyanamide [251], dialkyl phosphates [252], salicylate, thiosalicylate, benzoate, methionate and β-diketonate ions [216, 218-228]. As, it is well known that water bodies contamination by heavy metal has become one of the alarming problems in current time. Therefore, in this thesis, one objective was planned to design hydrophobic task specific ionic liquid comprising of metal coordinating groups. Designing such ionic liquids will add advantages like there is no need to add additional extractant that may have possibility of aqueous phase contamination. Moreover, the hydrophobic ionic liquid will itself act as biphasic solvent to water which will restrict the use of volatile organic solvent. The characterization of the TSILs synthesised for heavy metal extraction from aqueous phase will be done via different analytical techniques.

1A.10.1 Proposed Objectives:

[1] Synthesis of solvent responsive self-separative Brønsted acidic ionic liquid-polyoxometalate hybrids and exploring their catalytic activity on H_2O_2 mediated oxidation of alcohols.

[2] Developing ionic liquid based Keggin polyoxometalate hybrids as oxidative degradation catalyst of metobromuron in sunlight and discussing intermediates and its mechanistic aspects.

[3] Synthesizing variable alkyl bridged Brønsted acidic dicationic imidazolium ionic-liquid based phosphomolybdate hybrids and exploring its efficacy on one-pot sequential synthesis of 3-substituted indole.

[4] Investigative study on the dual functional behaviour of dicationic task specific imidazolium chloride ionic liquids as extractant as well as hydrophobic biphasic solvent in metal extraction from aqueous medium.

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Chapter-1B

Materials and Methodology

1B.1 General Information

This chapter demonstrates the general analytical techniques used for the characterization of synthesized ionic liquids (ILs) and ionic liquid-polyoxometalate (IL-POM) hybrids as well as the organic products. The structures of task specific ionic liquids (TSILs), IL-POM hybrids and organic products were confirmed using FT-IR, NMR (^{1}H, ^{13}C), CHN-elemental analyses. Additionally, for structure determination of the hybrids, ^{31}P NMR and ICP-OES analyses were performed along with the above-mentioned analyses. Melting point determination was done for the synthesized organic products. Thermal stability of the ILs were investigated using thermogravimetric analysis (TGA) and densities were measured using a pycnometer. The presence of Bronsted and Lewis acidic sites in the IL-POMs hybrids were investigated by FT-IR analysis using pyridine as a probe molecule. NH$_3$-TPD (Temperature programmed desorption) was also performed to understand the distribution of acid strength. Mass Spectrometry (MS) and High performance-liquid chromatography (HPLC) were used for product analysis and percentage conversion. Further characterizations of IL-POM hybrids were done using RAMAN, PXRD, SEM, EDX, and UV-Visible diffuse reflectance spectroscopy (UV-DRS). Atomic absorption spectroscopy (AAS) technique was performed for determination of Pb(II) concentration in water sample while investigating the metal extraction efficiency of 1,1'(butane-1,4-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium) chloride and named 1,1'(dodecane-1,12-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride TSILs, as biphasic metal extracting solvents.

1B.2 Materials used

All chemicals required for our study were purchased from various commercial suppliers like MERCK, Alfa Aesar and TCI chemicals and no further purification were done before use.

1B.3 Analytical methods of characterization

The various analytical methods used in the characterization of the TSILs, IL-POM hybrids, organic products are listed below:

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

The FT-IR spectra of all the liquid as well as solid samples were recorded on Perkin Elmer MIR-FIR FT-IR spectrophotometer. Presence of -SO₃H, -COOH functional groups in the respective ILs and IL-POM hybrids were studied using FT-IR spectroscopy. Moreover, information regarding presence of characteristic peaks of POMs in the fingerprint region (700-1200 cm⁻¹) was obtained from the FT-IR spectra [1,2]. FT-IR spectra also depict possible vibrations of different functional groups and bonds in the TSILs as well as IL-POM hybrids. Mechanism of Pb(II) ion extraction into the IL phase from aqueous medium was also studied comparing the FT-IR spectra of the metal unloaded IL phase to metal loaded ionic liquid phase. FT-IR studies provided valuable information regarding inter or intra molecular hydrogen bonding interactions. FT-IR spectra also information regarding availability of Bronsted and Lewis acidic sites in the synthesized IL-POM hybrids using pyridine as a probe molecule. The coordination of pyridine probe molecule with the Lewis acidic sites of materials displays peak around 1480 to 1490 cm⁻¹. Similarly peaks around 1530-1550 cm⁻¹ are displayed due to the interactions of the pyridine with the Brønsted acidic sites forming pyridinium ion [3].

1B.3.2 Nuclear Magnetic Resonance Spectroscopy (NMR) analysis

The NMR spectra (^{1}H NMR, ^{13}C NMR) of all the synthesized ILs, IL-POMs as well organic products (chalcones, Michael adducts) were recorded on JEOL 400 MHz spectrophotometer (δ in ppm) using DMSO-d_6 or CDCl$_3$ as solvent and TMS as internal standard. The ^{31}P NMR of synthesized IL-POMs were taken to understand the change in dynamic hydration environment around the phosphorus atom compared to the parent heteropoly acids.

1B.3.3 CHN elemental analysis

The elemental analysis of the synthesized TSILs, IL-POM hybrids as well as organic products were done using CHN PerkinElmer 20 analyser.

1B.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was done using Shimadzu TGA-50 analyser. The thermal stability of the synthesized ILs and the IL-POM hybrids were done till 600 ºC. The study allowed us to determine the water content in the ILs, IL-POM hybrids. And also step wise degradation of the organic moiety in the ILs as well as in the hybrids with temperature was also observed. It also allowed us to estimate the number of protons of the POM exchanged against the number of ionic liquid cations in the synthesized IL-POM hybrids.

1B.3.5 Raman Spectroscopy analysis

The Raman spectra of the synthesised IL-POMs were recorded in RENISHAW BASIS SERIES spectrophotometer with 514 green Argon ion laser of excitation wavelength 514nm. A detailed information regarding characteristic bands of Keggin anion can be obtained from the spectral data.

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

Powder X-ray diffraction spectra of IL-POMs and pure heteropolyacids (Chapter-2, 3) and PbO (Chapter-5) were recorded using model D8 FOCUS and MINIFIEX; BRUKER AXS, GERMANY and Rigaku Corporation, Japan. This diffraction spectra provided information regarding the peak shifting that occurred in IL-POM hybrids because of incorporation of ionic liquid cations into the Keggin anion. The structural transformations of the IL-POMs with different cation sizes were detected by powder X-ray diffraction in Chapter 2 and 3. Moreover, this technique was also used to confirm the formation of PbO, back extracted from the Pb(II) loaded ionic liquid phase in the metal extraction experiment in Chapter 5. 9KW Powder X-Ray Diffraction System, Make: Rigaku Technologies, JAPAN, Model: Smartlab was used to record diffraction spectra for [DILPOM]-1/2/3 and 12-molybdophosphoric acid in Chapter-4.

1B.3.7 UV-Visible Diffuse Reflectance Spectroscopy

The UV-Vis DRS measurements for the hybrids were conducted in solid state. First $BaSO_4$ was run as a blank sample UV-Vis diffuse reflectance as it was taken as reference. 25 mg of each sample was well ground with 0.5 g of $BaSO_4$ and then spread uniformly into the sample plate. Thus, the UV-Vis diffuse reflectance spectra was recorded in solid state without use of any solvent for all the synthesized IL-POM hybrids. The electronic spectra of the synthesized IL-POM hybrids were recorded in Shimadzu 2450 spectrophotometer with diffuse reflectance apparatus and also with Shimadzu UV-2600i spectrophotometer. The transitions due to excitation of electrons from 2p orbitals of oxygen to 3d orbitals of polyoxometalates are observed in all the synthesized IL-POM hybrids. Tauc plot for only $[DBDSA]_3PW_{12}O_{40}$ and $[DBDSA]_3PMo_{12}O_{40}$ were drawn to find the band gap value of the synthesized IL-POMs using the following equation:

$(\alpha h\upsilon)^{1/n} = \beta(h\upsilon - E_g)$ $\qquad$ **(Equation 1B.1)**

Here, α is the absorption coefficient, h is the Planck's constant, υ the frequency of incident photon, β is constant of band tailoring parameter, Eg the band gap energy [4]. Band gap can be calculated for direct (n = 1/2) or indirect transition (n = 2) and the power factor of transition mode 'n' is dependent on nature of solid material. A graph of $\alpha h\upsilon^2 (eV/cm)^2$ vs. Photon energy hυ (eV) is plotted to find Eg. A straight-line tangent from the obtained curve is drawn. The intersection point of the tangent and the x-axis are the band gap energies of the solid materials synthesized.

1B.3.8 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis

Scanning electron microscopy (SEM) images of the prepared IL-POM hybrids were acquired from JEOL JSM-6390LVSEM in addition to energy-dispersive X-ray (EDX) images. Information about the surface morphology of the hybrids were obtained from the SEM images. Changes in the surface morphology of the hybrids with varied cations were studied from the SEM images. EDX analysis technique gave information regarding the constituent elements of the IL-POM hybrids. EDX and EDS (Energy Dispersive Spectrometer) are two terms used for the same method. EDX generally refers to the method while EDS refers to the equipment. The analysis method of the instrument is based on generation of characteristic X-rays and is associated to electron microscopy.

1B.3.9 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The metal content in $[DEDSA]_3PW_{12}O_{40}$, $[DBDSA]_3PMo_{12}O_{40}$, $[DBDSA]_3PW_{12}O_{40}$, $[DBDSA]_3PMo_{12}O_{40}$ were analysed using ICP-OES analytical technique. This technique uses plasma as source and high resolution optics to isolate the specific emitted wavelengths for the different elements that needs to be detected and thus relative amount of elements present in the compound is obtained. It was done on Perkin Elmer, USA, Model: AVIO 220 MAX.

1B.3.10 Melting point measurements

The melting point of the organic products (chalcones, Michael adducts, IL-POM hybrids and 1,1'(dodecane-1,12-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride were recorded on BUCHI M-560 digital melting point.

1B.3.11 High Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography (HPLC), was used to study the oxidation of alcohols into aldehydes using $[DEDSA]_3PW_{12}O_{40}$ and $[DEDSA]_3PMo_{12}O_{40}$ as catalyst in presence of H_2O_2 as oxidant. The same chromatography was also used for monitoring the degradation of metobromuron using $[DBDSA]_3PW_{12}O_{40}$ and $[DBDSA]_3PMo_{12}O_{40}$ as catalyst in presence of H_2O_2 as oxidant. The HPLC instrument used for the study is equipped with UV visible detection-2489, refractive index detector-2414, HPLC Pump-515. Monitoring of oxidation reaction was done by HPLC method using C_{18} reverse phase column and UV detector at 254 nm. Equal mixture of water and acetonitrile was employed as mobile phase at a flow rate of 1 mL/min. However, monitoring of degradation of metobromuron was done by HPLC method using C_{18} reverse phase column and UV detector at 245 nm. 30:70 mixture of water and methanol was employed as mobile phase at a flow rate of 1 mL/min.

1B.3.12 Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) sample analysis were done using instrument with model CLARUS 600, Perkin Elmer analyzer. Information regarding the aldehyde products obtained in oxidation of alcohols using $[DEDSA]_3PW_{12}O_{40}$ and $[DEDSA]_3PMo_{12}O_{40}$ were obtained from the GC-MS spectra. Additionally, the degradation of metobromuron into various intermediates were identified from the GC-MS spectra obtained after analyzing the degraded solution.

1B.3.13 Total Organic Carbon

Total organic carbon (TOC) present in the metobromuron herbicide samples before and after degradation were analyzed by Total Organic Carbon Analyzer, Shimadzu Scientific instruments, TOC-LCSH.

1B.3.14 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) was used to detect metal content in the extraction study of Chapter 5. The concentration of Pb(II) in aqueous phases after and before extraction were determined by atomic absorption analysis (AAS, Thermo Scientific, UK, AAS-ICE 3500). The concentration measurement of metal was done in triplicate and extraction efficiency was calculated with 95% confidence interval. Characteristic

wavelengths of electromagnetic radiation from a light source are applied through the metal ion containing liquid aqueous sample and thus absorption of wavelengths differently by metals will generate absorbances. These absorbances data are measured against standards of metal of interest. The following formulas are used for calculations of E% (Extraction Efficiency), D (Distribution ratio):

$$E\% = [(C_i)_{aq} - (C_f)_{aq} /(C_i)_{aq}] \times 100 \qquad \textbf{(Equation 1B.2)}$$

$$D = [(C_i)_{aq} - (C_f)_{aq} /(C_f)_{aq}] \qquad \textbf{(Equation 1B.3)}$$

Here C_i and C_f are the initial and final concentration of metal ions in aqueous medium.

1B.3.15 pH meter

The pH values of the aqueous phase were determined by a model Eutech pH meter 700 (Thermo Scientific, USA), which was calibrated by the standard buffer solutions with pH 4.00, 7.00 and 9.13.

1B.3.16 NH₃-Temperature Programmed Desorption Analysis

NH$_3$-TPD analysis of [DILPOM]-1/2/3 were carried out in ChemBET Pulsar TPR/TPD, Automated chemisorption Analyzer, Quantachrome instruments.

1B.3.17 The Brunauer - Emmett – Teller (BET) Analysis

The Brunauer - Emmett – Teller (BET) analysis was performed to investigate the surface area data of the [DILPOM]-3. The BET surface area of [DILPOM]-3 was determined using nitrogen (N$_2$) sorption data measured at 77K using using Surface Area and pore size analyzer Make: Quantachrome Instruments, Model: Autosorb, IQ MP.

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