Chapter 5A

Review on poly(ethyleneglycol) linked dicationic ILs and formation of 5-hydroxymethylfurfural using ionic liquids

5A.1. Geminal dicationic ionic liquids

The review of multi-charged ILs in **Section 1A.3**:**Chapter 1A**, describes various superior physical properties of multi-charged ionic liquids (ILs) as compared to traditional ILs in terms of thermal stability and their presence in liquid phase at wide temperature range (e.g. -4 ^{o}C to 400 ^{o}C) [1]. Geminal dicationic ILs with different charged heads and spacers have been utilized to prepare ionic liquid material of varied physical and chemical properties for further uses as solvents in high-temperature reactions [2-4], high-temperature lubricants [5] and ultrastable separation phases [6-8], extraction process [9, 10] and mass spectrometry unlike ordinary ILs [11-13]. Furthermore, attachment of one or more acidic sites to the cation may convert them to acidic ILs catalyst or medium for acid catalyzed organic reactions without disturbing the basic characteristics of ILs.
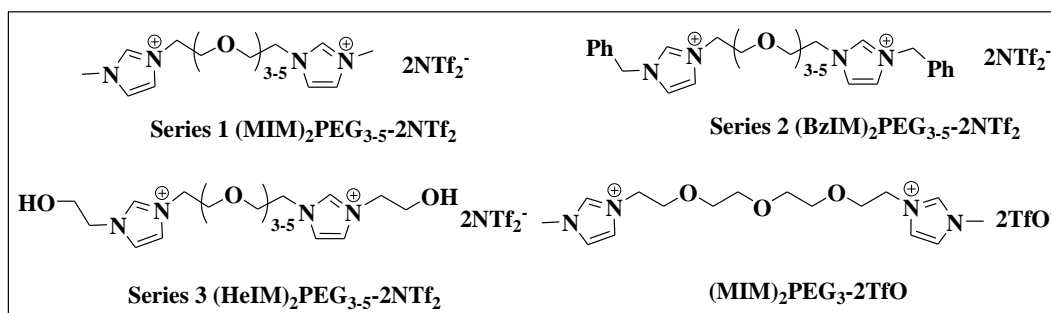
5A.2. Poly(ethylene glycol)-linked dicationic imidazolium and ammonium ionic liquids and their uses as solvent/catalyst systems

Ionic Liquids and poly(ethylene glycol) (PEG) have individually been explored as potential reaction medium in recent decades and experienced tremendous explosion in applications. They have been distinguished from the classical organic solvents by considering their intrinsic physical and chemical properties. The use of PEG for immobilization of reagents and catalysts have extensively been explored for synthesis of functionalized supported materials due to their distinctive properties, such as inexpensive, nontoxic, nonvolatile, thermally stable, environmentally benign [14, 15]. The poly(ethylene glycol) functionalized ionic liquids (PEG-ILs), which incorporate the advantages of PEG and ILs, have demonstrated attractive physicochemical properties and application in various areas [16-18]. The transfer of unique "critical solution temperature" (CST) property of PEG to PEG-functionalized DILs have generated temperature-dependent biphasic ionic liquid systems in organic solvent which promise them the possibility of efficient recovery as recyclable catalysts or reaction medium. For example, two poly(ethylene glycol)-bridged dicationic ionic liquids such as neutral PEG-DILs [19, 20] and acidic PEG-DAILs [21-27] have been explored as powerful reusable catalysts for organic reactions. The PEG-DAILs (or PEG-DILs) were found to have the temperature-dependent biphasic behavior in toluene in certain temperature [19,

24]. As solvent, they were used in dissolving carbohydrates and polymers [28], in protein and enzyme stabilization and activation [29], in partitioning inorganic salts from aqueous solutions [30], or in acting reductants and stabilizers for the synthesis of nanoparticles [31]. Through cation or anion modification, this class of IL can be designed as a new class of task-specific functional solvent and material with retention of the characteristics exhibited by the parent counter ion. Among the PEG functionalized IL (IL_{PEG})s, those functionalized with polyfluoroalkyl substituents were employed as high temperature lubricants [32], those with alkyl or hydroxyalkyl substituents on the imidazolium ring were used as stationary phases in analytical chromatography systems [33], IL_{PEG} with a azabicyclo cationic moiety was used in CO_2 absorption studies [17] and acidic ILs were also applied in biomass conversion process [34].

The physicochemical properties of the IL_{PEG} depend on the cation structure, nature of the counter anion as well as on the number of the ether unit in the PEG chain. From the results obtained in case of ILs with long PEG chains, the number of ether units in the PEG chains was expected to influence the intermolecular interaction, chain flexibility and conformation of the ILs [35, 36]. Accordingly, the rheological behavior, ionic conductivity and thermophysical properties of these ILs can be finely tuned for specific applications [37-39].

Huang et al. [33] in 2007 for the first time reported a series of PEG-bridged imidazolium geminal DILs (**Fig. 5A.1**) as potential Gas Chromatography (GC) stationary phases for efficient separation of several mixtures of flavor and fragrances containing 24 components of different polarities. The authors prepared the $(MIM)_2PEG_{3-5}-NTf_2$ and $(BzIM)_2PEG_{3-5}-NTf_2$ ILs according to a reported procedure [5]. They evaluated their thermal stabilities and molecular interaction parameters. This study indicated comparable or higher resolving power of these ILs as stationary phases compared to other polysiloxane and poly(ethylene glycol)-based stationary phases. These IL were also found to be thermally very stable.

Fig. 5A.1: Structure of PEG bridged germinal DILs

Ren and Cai [19] in 2008 employed this PEG linked imidazolium based dicationic IL (**Fig. 5A.2**) as efficient recyclable reaction medium for protection of aldehydes and ketones with ethylene glycol in presence of iodine as catalyst at room temperature. The IL showed biphasic behavior with toluene at lower temperature.
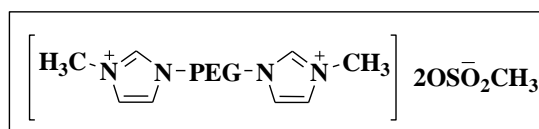

Fig. 5A.2: Structure of PEG linked imidazolium based dicationic IL

Zeng et al. [32] in the same year prepared a series of alkyl substituted imidazolium based polyalkylether bridged dicationic ILs with simple anions such as NTf_2^-, BF_4^- and PF_6^- via **Scheme 5A.1**. They also used other three bridging group in between the alkyl substituted imidazolium cations namely 1, 4-bismethylenebenzene, or 1, 4-bismethylene-2, 3, 5, 6-tetrafluorobenzene for modification of physicochemical properties of the bridged geminal dicationic ILs. As the length of alkyl substituent of imidazolium cation increases their melting points also increase containing a common linker and anion, whereas the densities decrease concomitantly. The ILs displayed good high-temperature tribological characteristics at 300 °C, meeting one of the criteria for high temperature lubricants.

In 2009, Zhi et al. [40] developed acidic PEG-1000 linked imidazolium dicationic IL (PEG$_{1000}$-DAIL) via **Scheme 5A.2**. It showed biphasic behavior with toluene at low temperature. This PEG$_{1000}$-DAIL/toluene system was efficiently utilized as acidic catalyst/solvent system for the synthesis of 5-oxo-5, 6, 7, 8-tetrahydro-4H-benzo[b]pyrans by three-component condensation reaction of aromatic aldehydes,

malononitrile (or ethyl cyanoacetate) and 5, 5-dimethyl-1, 3-cyclohexanedione at 80-90°C (**Scheme 5A.3**).

Fang et al. [24] in 2011 employed the above PEG-1000 based acidic dicationic IL as recyclable temperature-dependant phase-separation catalytic system in conjunction with propylene glycol monomethylether for the synthesis of 2, 4, 5-trisubstituted imidazoles via one-pot three-component condensation with various aldehydes, benzil and ammonium acetate in reasonable to good yield of 81-95% (**Scheme 5A.4**). The reaction was carried out homogeneously at 70 °C, while at room temperature it forms a biphasic system. The catalytic system could be successfully reused up to eighth cycles without significant decrease in catalytic activity.
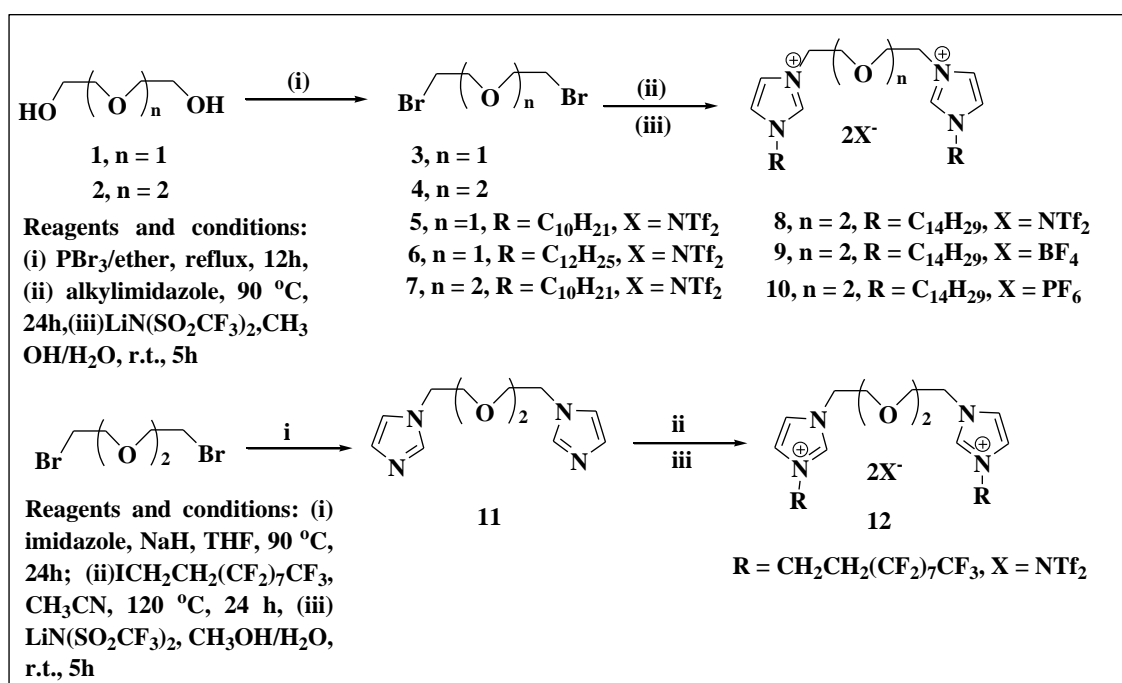

Scheme 5A.1: Synthesis of PEG functionalized dicationic ILs with C_{10}-C_{14} alkyl or $C_8F_{17}C_2H_4$ substituents
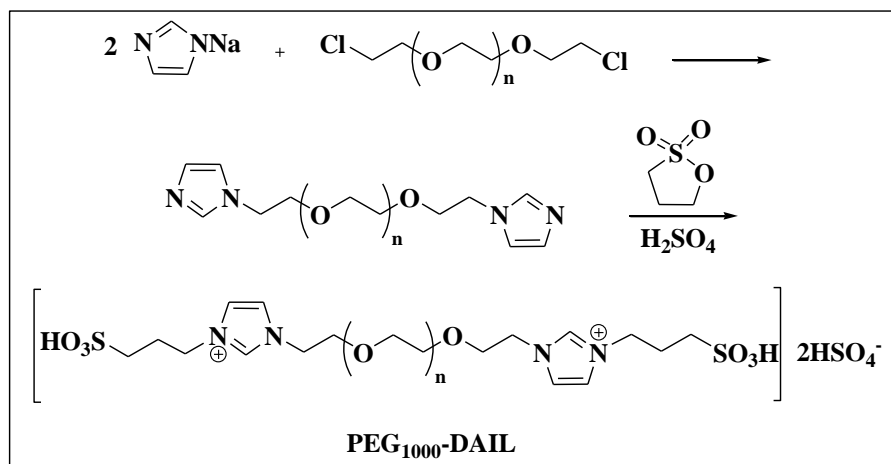
**Scheme 5A.2**: Preparation of PEG$_{1000}$-DAIL
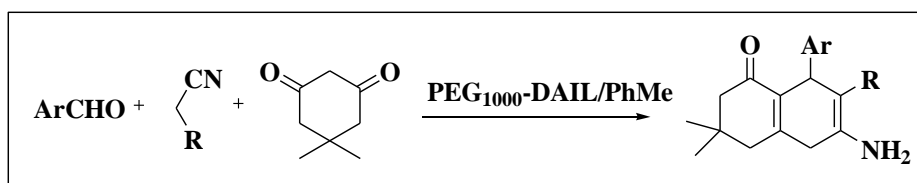
Scheme 5A.3: Synthesis of 5-oxo-5, 6, 7, 8-tetrahydro-4H-benzo[b]pyrans
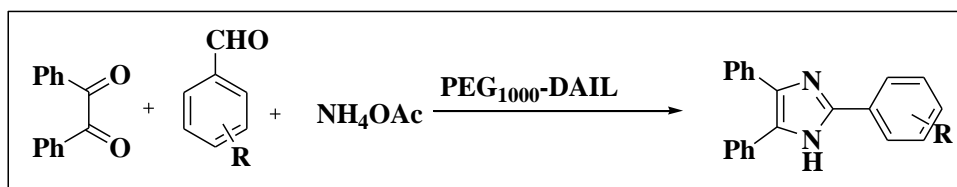
**Scheme 5A.4**: Synthesis of 2, 4, 5-trisubstituted imidazoles catalyzed by PEG$_{1000}$-DAIL

Lou et al. [41] again in 2011 used the same acidic PEG 1000-based DIL as reusable catalyst for preparation of amidoalkyl naphthols via three component condensation of aldehydes (**Scheme 5A.5**) with amides and 2-naphthol at 80 ^{o}C in neat condition within 3-15 min to give excellent yield of product.
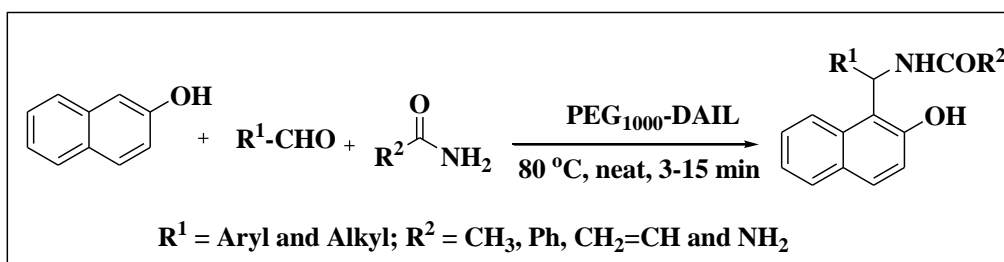
Scheme 5A.5: Synthesis of amidoalkyl naphthols catalyzed by PEG$_{1000}$-DAIL

Wang et al. [27] in 2013 developed poly(ethylene glycol) linked neutral dicationic ionic liquids (PEG-DILs)/toluene/p-TsOH (**Scheme 5A.6**) and the above PEG$_{1000}$-DAIL/toluene as recyclable temperature-dependent biphasic catalyst combined reaction media system at 80 °C for esterification of aromatic acids and acetalization of aromatic aldehydes with good to excellent yields (**Scheme 5A.7**).
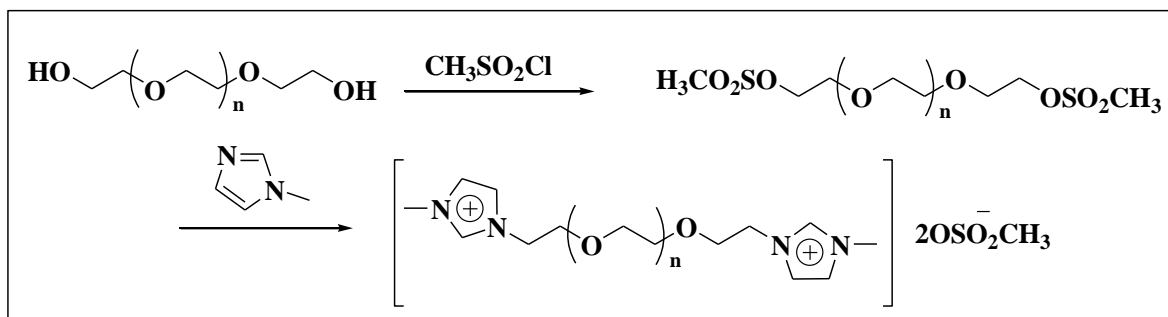

Scheme 5A.6: Synthesis of PEG-DILs by Wang et al.
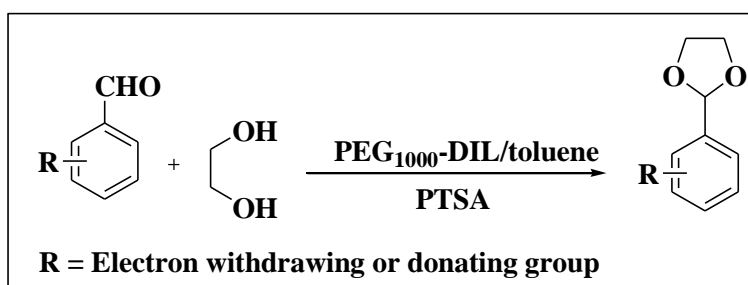
**Scheme 5A.7**: Acetalization in PEG$_{1000}$-DIL/toluene/PTSA catalytic system

The two dicationic ionic liquids, PEG-DILs and PEG-DAILs (**Fig. 5A.3**) were again investigated by Ren et al. [23] in 2015 as recyclable and chemoselective catalysts for facile protection of carbonyl compounds to oxathiolanes and thioacetals at 80 °C in toluene (**Scheme 5A.8**).
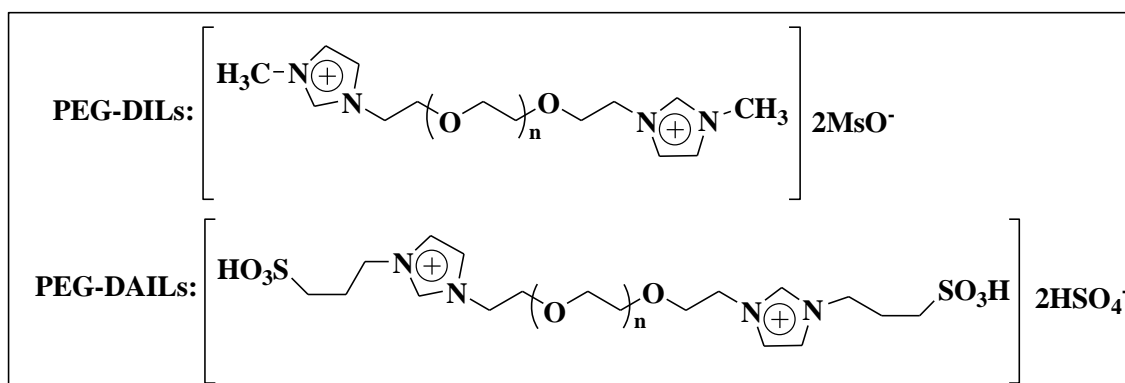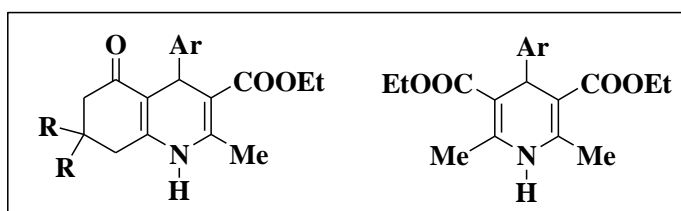

Fig. 5A.3: Structure of PEG-DIL and PEG-DAIL

R^1 = alkyl or aryl; R^2 = H or alkyl or aryl; X = O or S
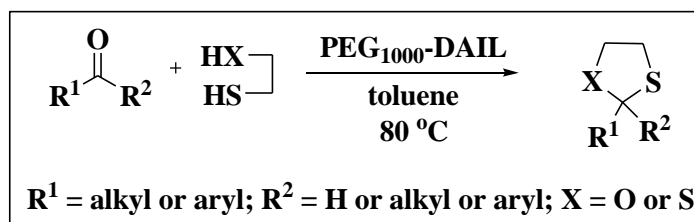
Scheme 5A.8: Conversion of carbonyl compounds to oxathiolanes and dithioacetals catalyzed by PEG$_{1000}$-DAIL

He also utilized the acidic PEG$_{1000}$-DAIL as efficient catalyst for one-pot synthesis of 1, 4-dihydropyridines (**Fig. 5A.4**) via Hantzsch reaction in toluene at 80 ^{o}C [22].


Fig. 5A.4: Structure of 1, 4-dihydropyridine derivatives

Lu et al. [42] in 2015 also performed aerobic oxidation of toluene derivatives to corresponding acids successfully in PEG$_{1000}$-DAIL as solvent and N, N, N-trihydroxyisocyanuric acid (THICA)/MnO$_2$ as oxidant system. It is explained that THICA/MnO$_2$ is very active and selective and several toluene derivatives are efficiently oxidized to corresponding acids under mild conditions. Both the catalyst and PEG$_{1000}$-DAIL can be reused after simple separation.

In 2013, Luo et al. [43] prepared poly(ethylene glycol) bridged tertiary amine functionalized ionic liquid PEG$_{800}$-DPIL(Cl) according to **Scheme 5A.9**. The synthesized IL was able to form a temperature driven reversible biphasic system with cyclohexane/isopropanol mixed solvent. This system was utilized as a facile catalyst and co-solvent in Knoevenagel condensation to afford substituted benzylidenes in excellent yields. At the end of the reaction, it could be recovered by simple decantation and reused several times.
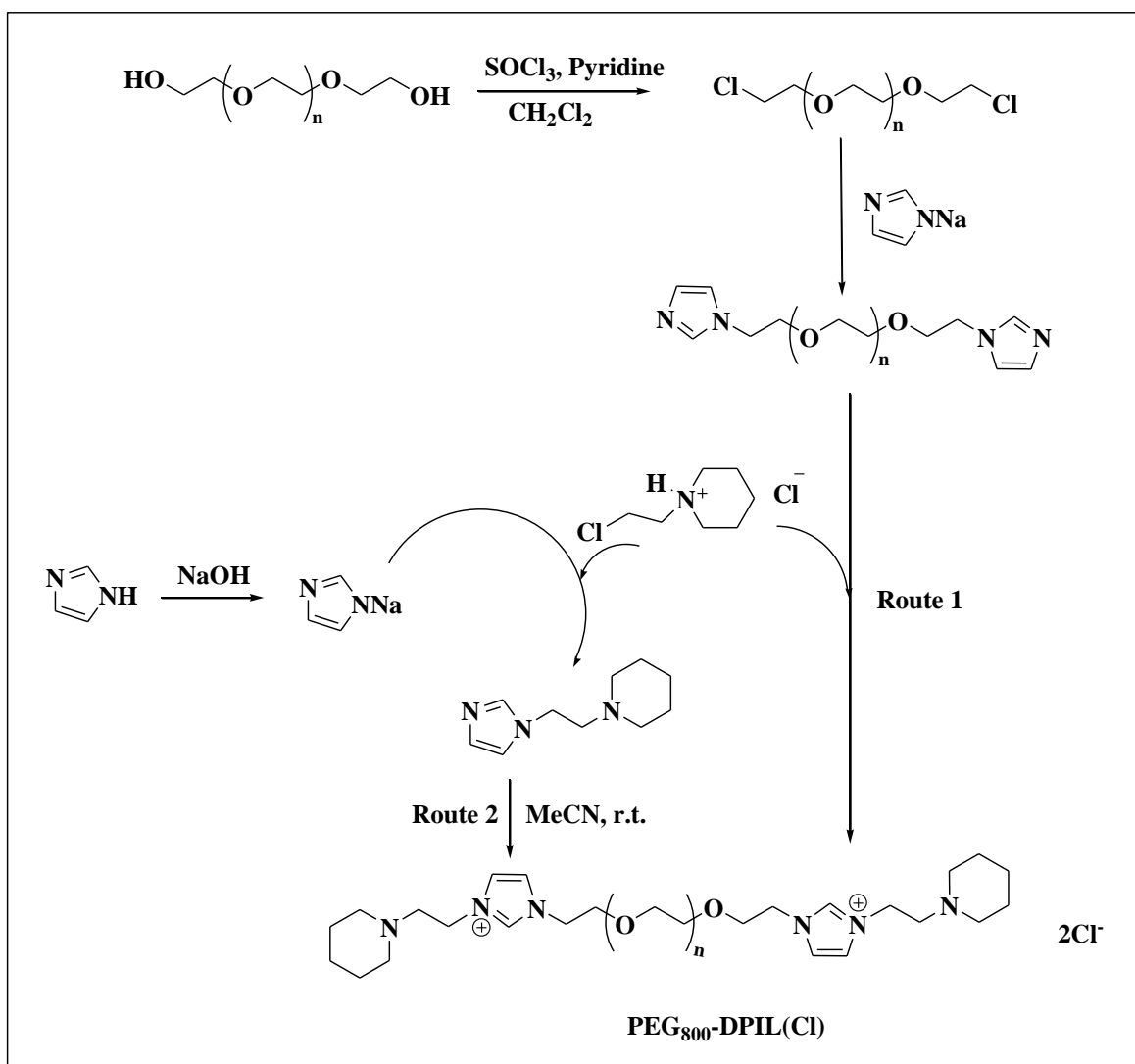
Scheme 5A.9: Preparation of piperidine functionalized PEG$_{800}$-DPIL(Cl)

The piperidine functionalized PEG$_{800}$-DPIL(Cl) was again utilized by the same group for catalytic conversion of four component Hantzsch reaction under solvent-free conditions to afford hydroquinolines with high to excellent yields (**Scheme 5A.10**) [44]. The IL could be easily recovered by simple work up and reused for next eighth cycles without significant loss in activity.

Wang et al. [45] developed a novel 8-hydroxyquinoline functionalized PEG-1000 bridged dicationic ionic liquid ([HQ-PEG$_{1000}$-DIL][BF$_4$]) according to **Scheme 5A.11** in the same year. The IL was efficiently applied as a recyclable ligand for copper-catalyzed N-arylation of nitrogen-containing heterocycles with aryl halides (**Scheme 5A.12**). The catalytic system was easily recycled for at least five times without obvious loss in activity.

Wang et al. [46] in 2013 described a method for preparation of diol-functionalized poly(ethylene glycol)-bridged dicationic ionic liquid ([diol-PEG$_{1000}$-DIL][PF$_6$]) (**Scheme 5A.13**). They explored the catalytic efficiency of this IL for copper-catalyzed amination of aryl iodides/ bromide with aqueous ammonia to afford the corresponding aromatic primary amines in good to excellent yields (**Scheme 5A.14**). The CuI/[diol-PEG$_{1000}$-DIL][PF$_6$] catalytic system could be efficiently recycled for next five cycles without loss in its activity.
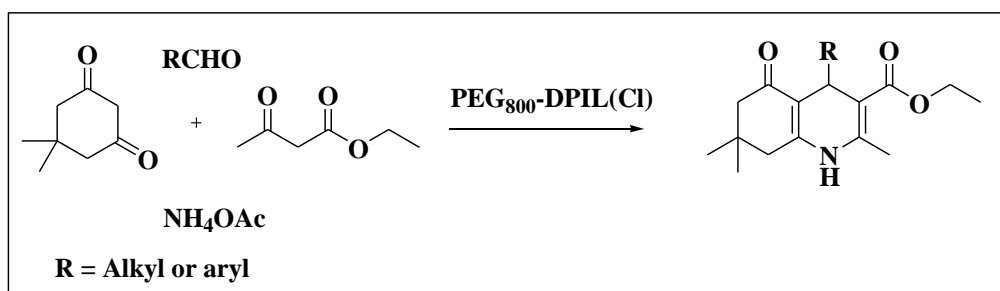
Scheme 5A.10: Synthesis of hydroquinolines catalyzed by PEG$_{800}$-DPIL(Cl)
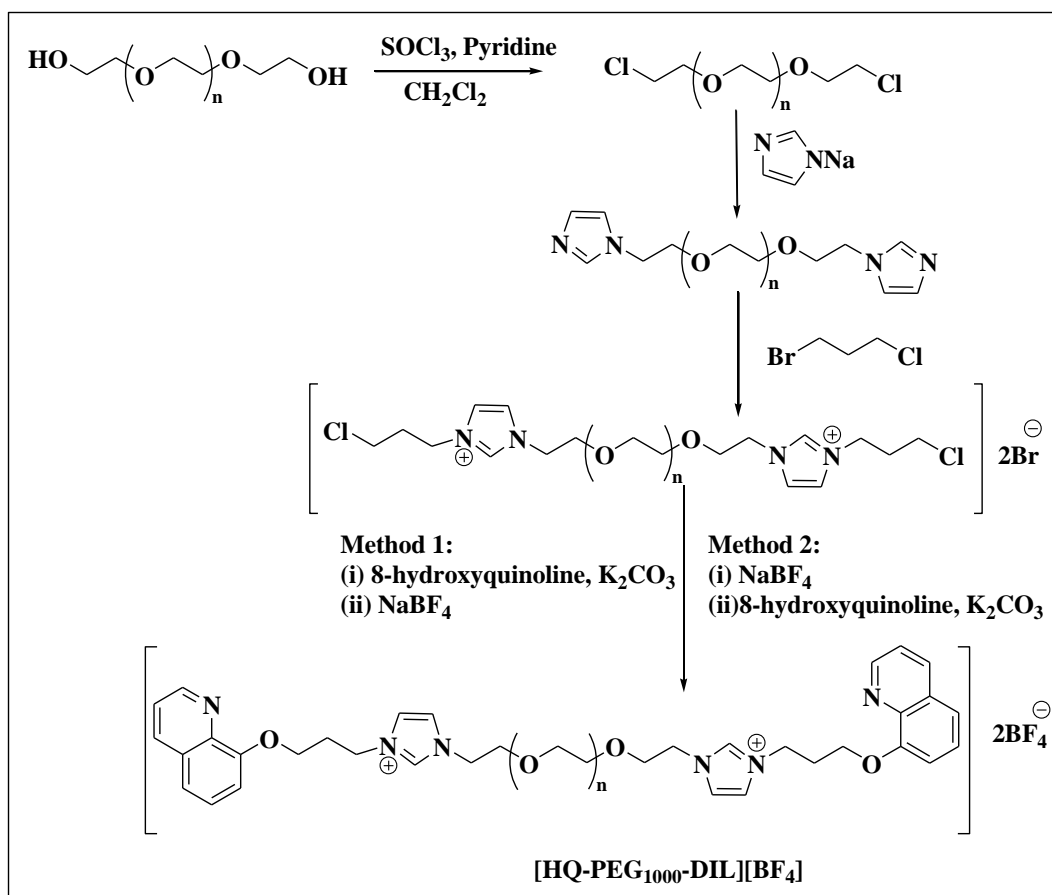
Scheme 5A.11: Preparation of [HQ-PEG$_{1000}$-DIL][BF$_4$]
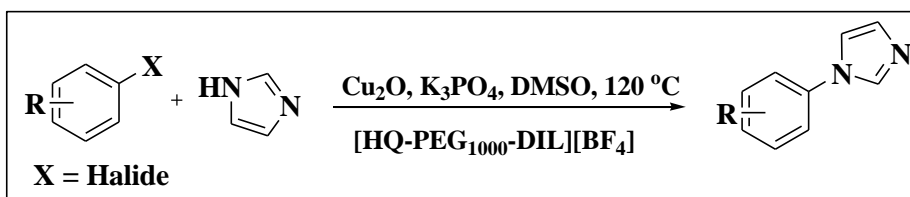
Scheme 5A.12: Copper-catalyzed N-arylation of nitrogen-containing heterocycles with aryl halides using the IL as recyclable ligand
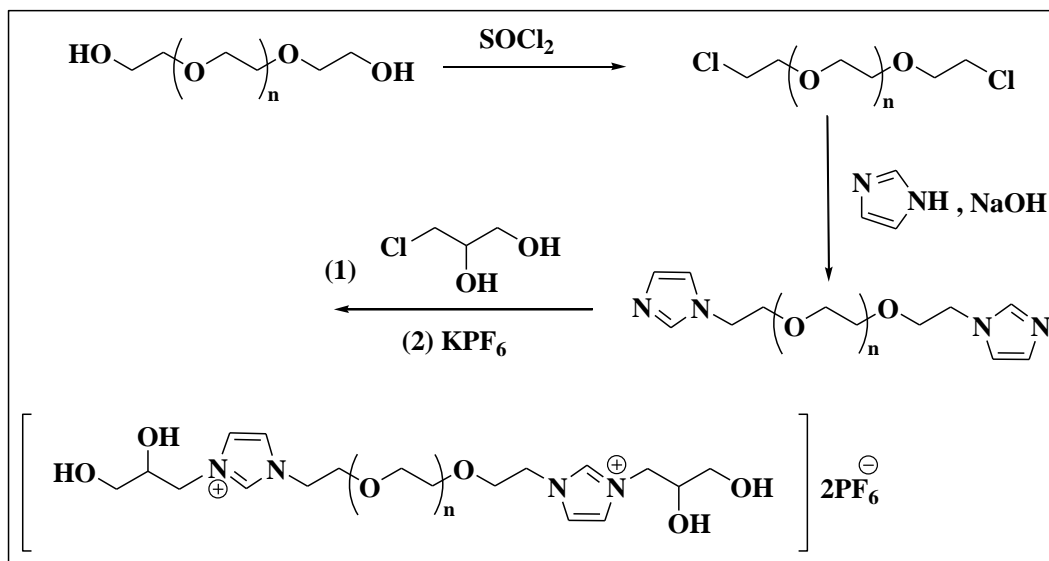
Scheme 5A.13: Preparation of [diol-PEG$_{1000}$-DIL][PF$_6$]

Wang et al. [47] reported a poly(ethylene glycol) bridged primary amine functionalized dicationic ionic liquid ([PA-PEG$_{1000}$-DIL][BF$_4$]) (**Scheme 5A.15**) and utilized as recyclable catalyst for the synthesis of substituted tetrahydrobenzo[b]pyrans (**Fig. 5A.5**) through a one-pot three-component condensation of aromatic aldehydes, dimedone and malononitrile within 10-30 min in water under reflux condition in 86%~96% yields.
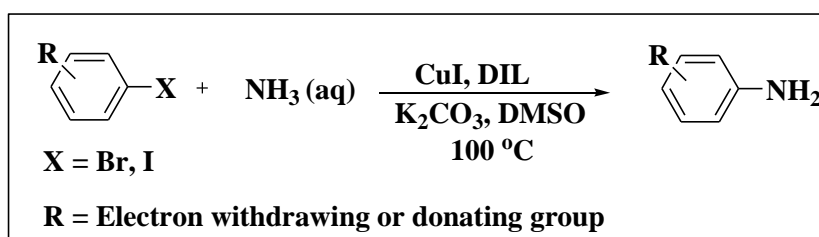
Scheme 5A.14: CuI/[diol-PEG$_{1000}$-DIL][PF$_6$] catalyzed amination of aryl iodides/ bromide with aqueous ammonia
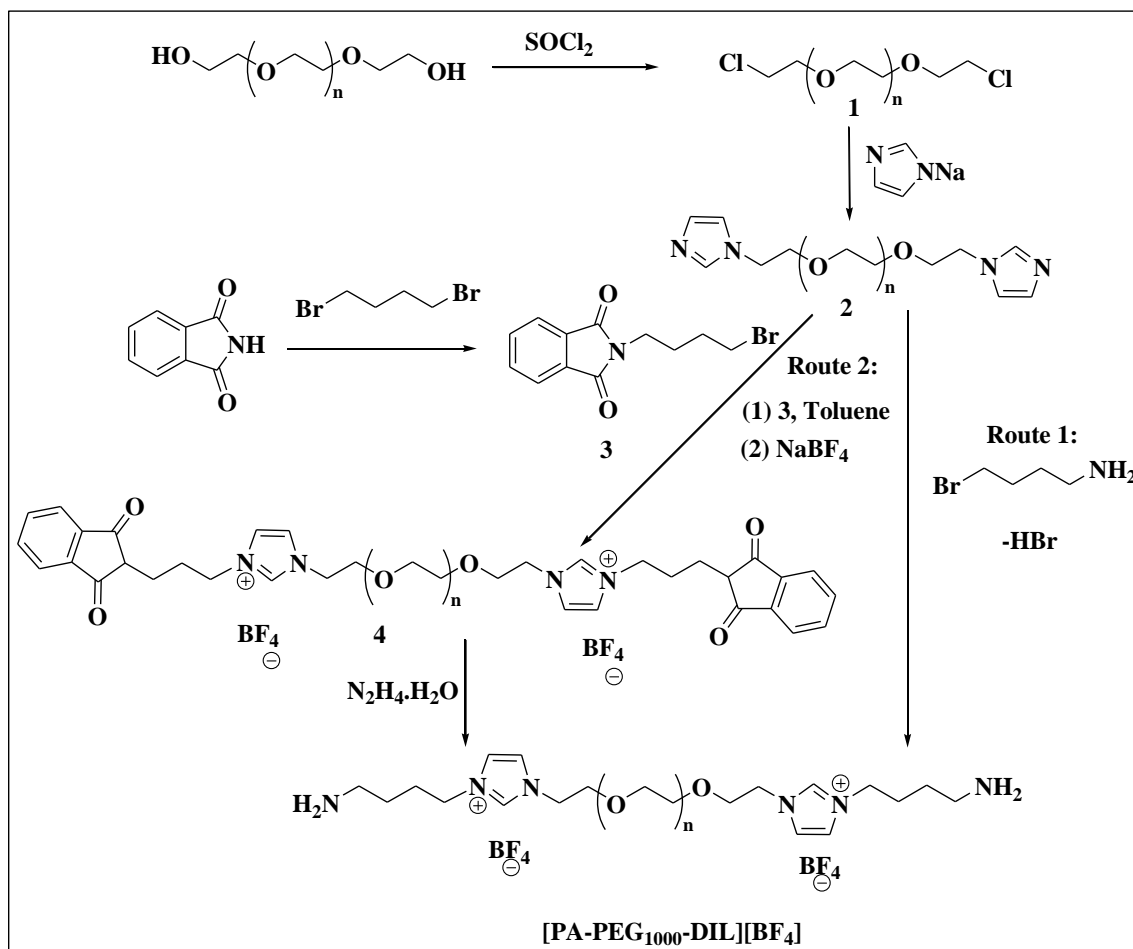
Scheme 5A.15: Preparation of [PA-PEG$_{1000}$-DIL][BF$_4$]

R = electron withdrawing or donating group
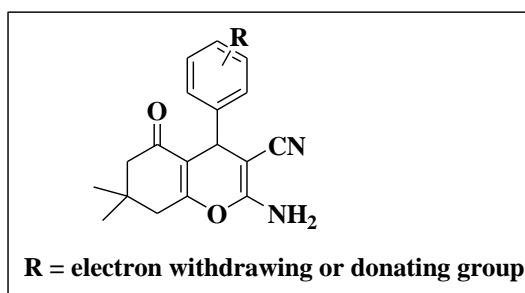
Fig. 5A.5: Structure of substituted tetrahydrobenzo[b]pyrans

Wang et al. [48] in 2013 prepared two salicylaldoxime-functionalized PEG bridged DILs: [salox-PEG$_{1000}$-DIL][BF$_4$] and [salox-PEG$_{1000}$-DIL][PF$_6$] using the reaction **Scheme 5A.16**. The [salox-PEG$_{1000}$-DIL][BF$_4$] was found to be an efficient and recyclable ligand for Pd(OAC)$_2$ catalyzed Suzuki-Miyaura reaction of substituted aryl halides with aryl boronic acid in water (**Scheme 5A.17**). It could be easily recovered and reused for next five runs with the same catalytic activity.
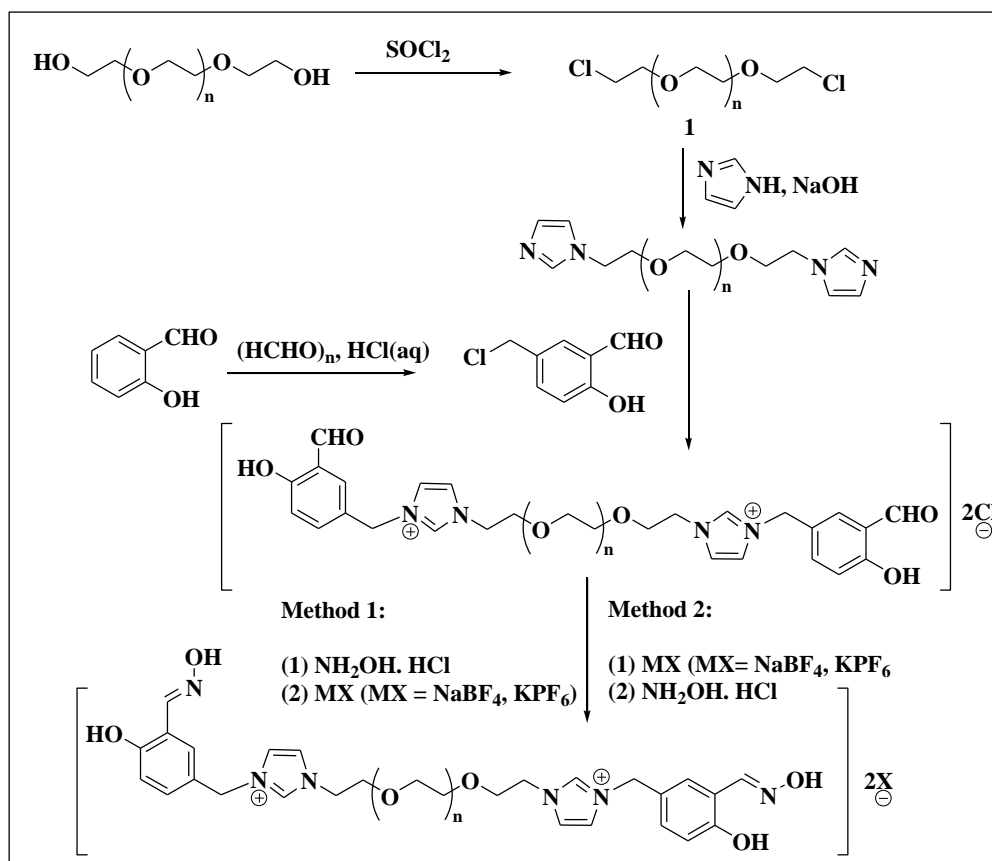
Scheme 5A.16: Preparation of [salox-PEG$_{1000}$-DIL][BF$_4$]/[PF$_6$]
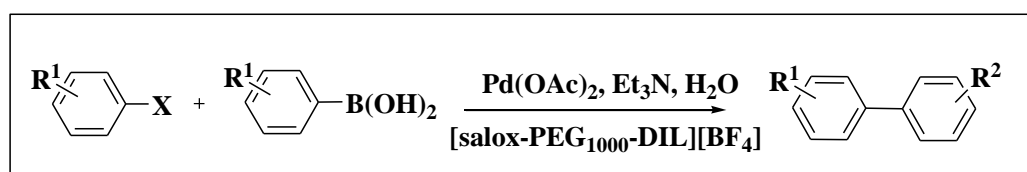
Scheme 5A.17: Suzuki-Miyaura reaction catalyzed by [salox-PEG$_{1000}$-DIL][BF$_4$]

Jadhav et al. [49] synthesized a series of unsymmetrical dicationic ILs based on imidazolium, pyridinium and triethyl ammonium cations in association with three anions such as HSO$_4^-$, CH$_3$SO$_3^-$, Br$^-$ (**Scheme 5A.18**). The catalytic efficiencies of these unsymmetrical ILs were evaluated in the dehydration of fructose into 5-hydroxymethylfurfural (HMF) in mild reaction condition. Among them, ([tetraEG(mim)(triethylamo)][HSO$_4^-$]$_2$) unsymmetrical IL exhibited the best catalytic activity with 100% fructose consumption and 92.3% HMF yield in 40 min reaction using 10 mol% of catalyst at 70 ^{o}C without any added solvent and catalyst. All these IL were able to selectively dehydrate fructose in to HMF in high yield.
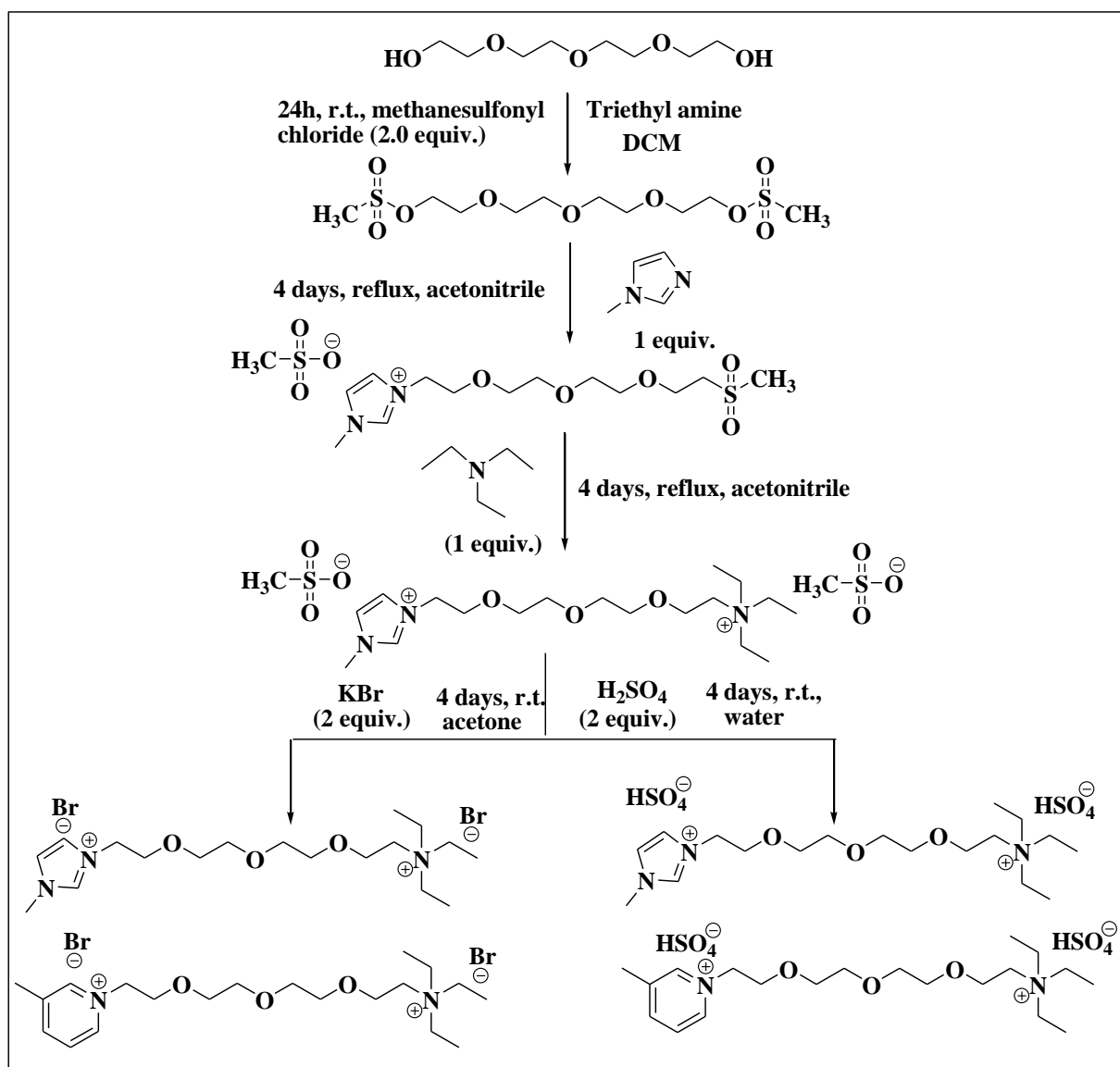
Scheme 5A.18: Preparation of unsymmetrical dicationic ILs by Jadhav et al.

In 2015, Godajdar and Ansari [50] reported a magnetic PEG-based dicationic ionic liquid PEG-MDIL (**Fig. 5A.6**) as phase-transfer catalyst for nucleophilic substitution reactions of benzyl halides in good to excellent yields at 90 °C in water (**Scheme 5A.19**). The IL possesses the advantage of being easily recycled and reused for several runs with identical catalytic activity for synthesis of benzyl azides and cyanides.

The same magnetic DIL, PEG-MDIL was exploited as phase transfer catalyst for aqueous synthesis of 1, 2-azidoalcohols via regioselective ring opening of 1, 2-epoxides with high yields under reflux within 15-20 min (**Scheme 5A.20**) [51].The product was obtained in pure state without further purification.
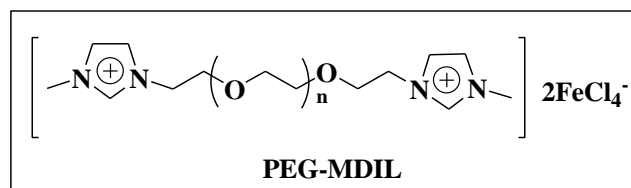
Fig. 5A.6: Structure of PEG-MDIL
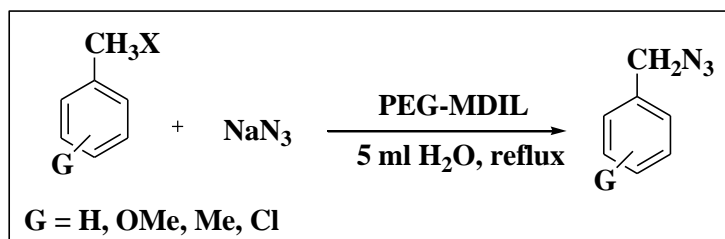
Scheme 5A.19: Synthesis of benzyl azides and cyanides catalyzed by PEG-MDIL
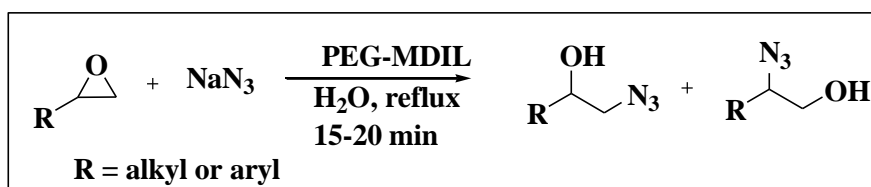
Scheme 5A.20: Synthesis of 1, 2-azidoalcohols catalyzed by PEG-MDIL

Liu et al. [52] synthesized a variety of PEG 400-functionalized dicationic acidic ionic liquids (ILs) (PEG_{400}-DAILs) (**Scheme 5A.21**) and tested for dehydration of fructose to HMF at 80-110 °C in various solvents. Among them, hydrogen sulfate anion-based ILs showed higher catalytic performance in the conversion of fructose. The highest HMF yield of 96.5% with 100% consumption of fructose was obtained after 60 min at 110 °C in DMSO. The used IL catalyst could be easily separated and recycled repeatedly with retention of identical catalytic activity.

Eshghi et al. [53] designed a benzimidazolium based-N-sulfonic group containing acidic dicationic IL (**Scheme 5A.22**) and investigated as reusable acidic catalyst for one-pot synthesis of α-aminophosphonates derivatives under solvent free conditions.

Jadhav et al. [54] prepared a series of symmetrical room temperature ionic liquids consisting of N-methylimidazolium rings linked with a short oligo(ethylene glycol) chain and bis-trifluoromethane sulfonimide (NTf_2^-) as anionic part by following the multi-step reaction **Scheme 5A.23**. The catalytic activity of these ILs was evaluated

in the esterification reaction of acids with alkyl halides in solvent-free conditions at room temperature within short period. Among the three type of catalysts, 0.1 equimolar of ([tetraEG(mim)$_2$][NTf$_2$]$_2$) was found to be, the most efficient and reusable catalyst for this reaction. The IL catalyst can be separated by a simple decantation method and regenerated several times.
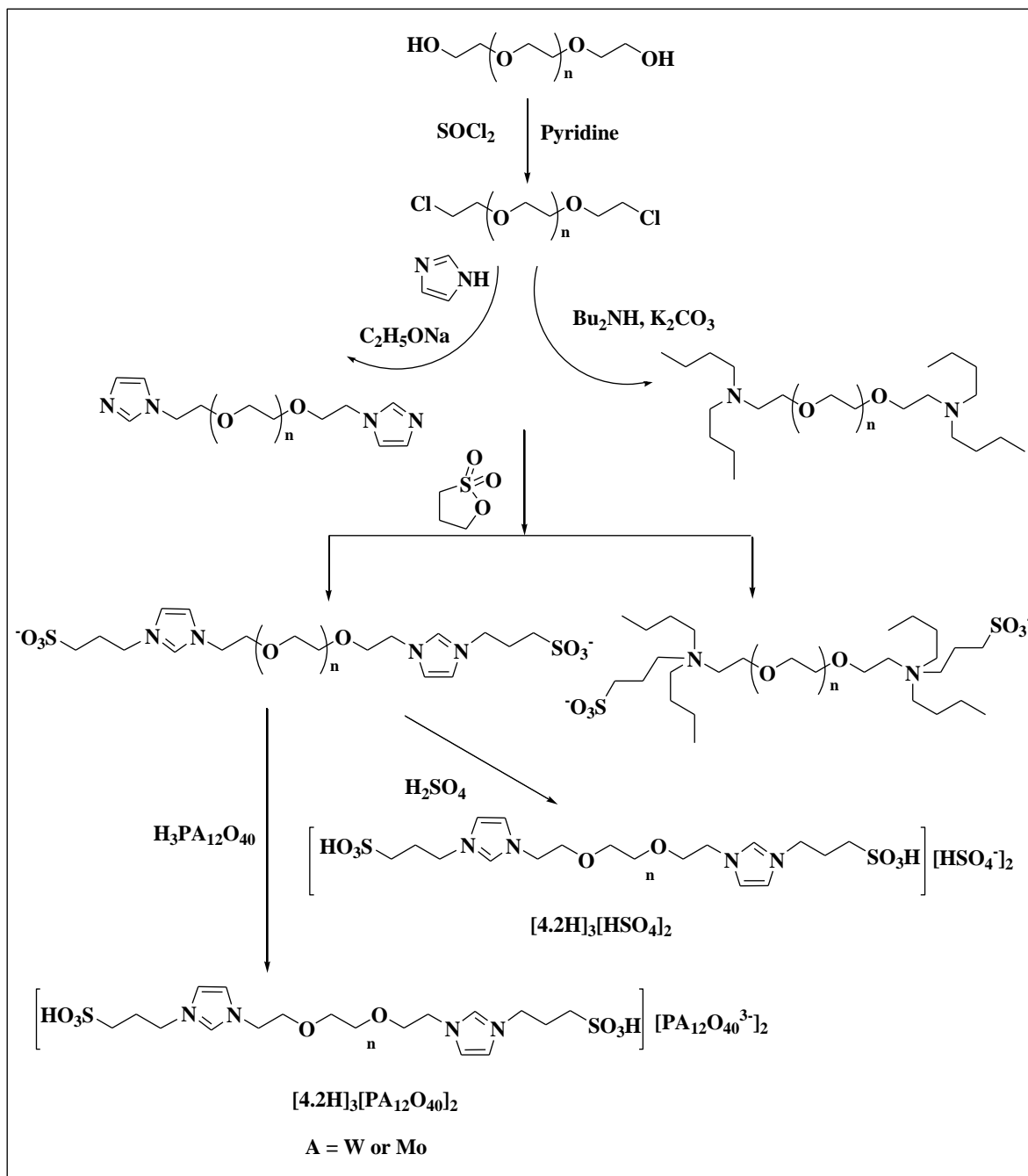
Scheme 5A.21: Preparation of PEG$_{400}$-DAILs by Liu et al.

In 2015, Jadhav et al. [55] designed hexaethylene glycol bis(3-hexaethylene glycolimidazolium) dimesylate (hexaEG-DHIM) as PEG-based dicationic IL (**Scheme 5A.24**) and used as highly efficient promoter for the nucleophilic hydroxylation of alkyl halides to the corresponding alcohol products in neat water media. The hexaEG-DHIM could be reused several times with the same catalytic activity and even base-sensitive and/or polar alkyl halide substrates were converted to the desired products with high chemoselectivity.
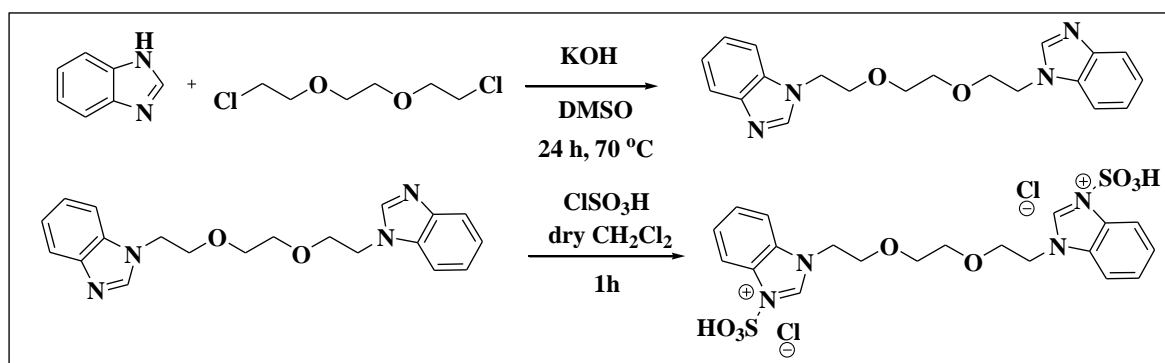
Scheme 5A.22: Preparation of benzimidazolium based dicationic IL
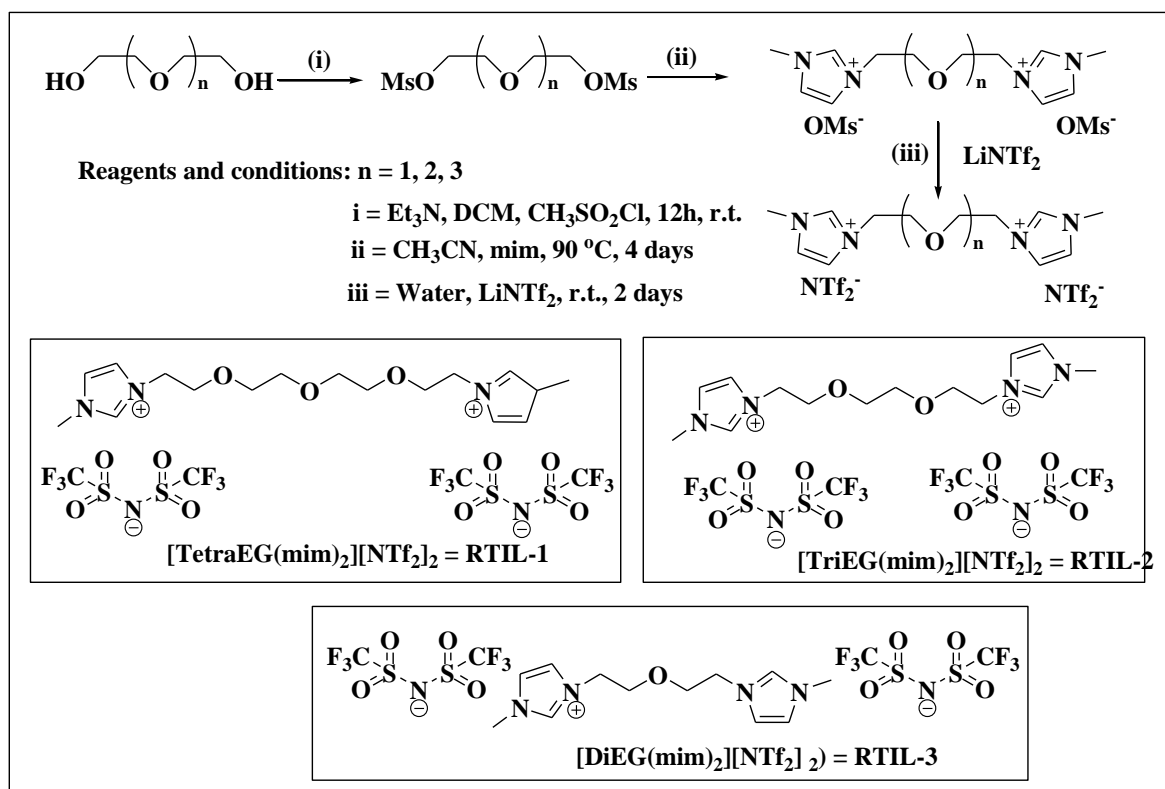
Scheme 5A.23: Preparation of symmetrical ILs by Jadhav et al.
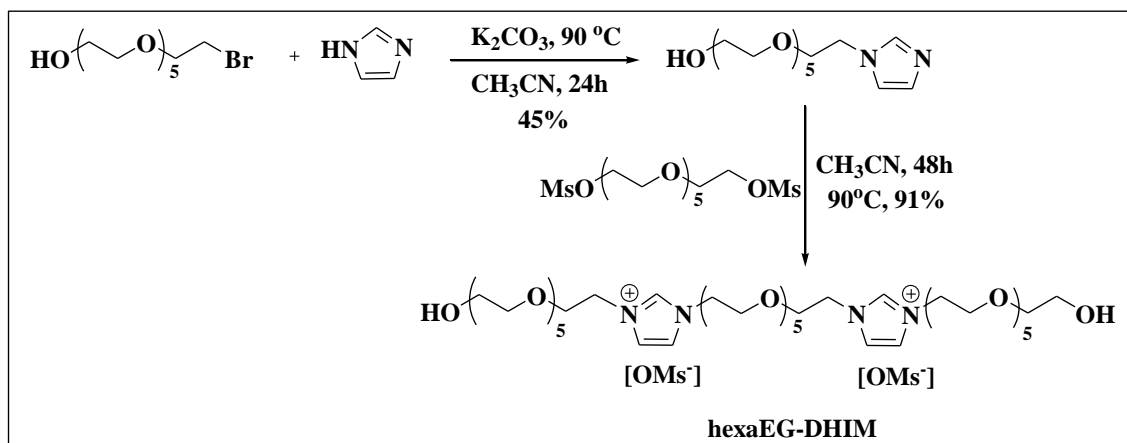
Scheme 5A.24: Preparation of hexaEG-DHIM

Wang et al. [56] introduced PEG bridged triethylamine functionalized dicationic IL ([TEA-PEG$_{800}$-DIL][Cl]) (**Fig. 5A.7**) and observed as recyclable catalyst for three-component synthesis of 2-amino-2-chromene derivatives in water under reflux temperature with excellent yields (**Scheme 5A.25**). The catalyst could with stand a wide variety of substrates.
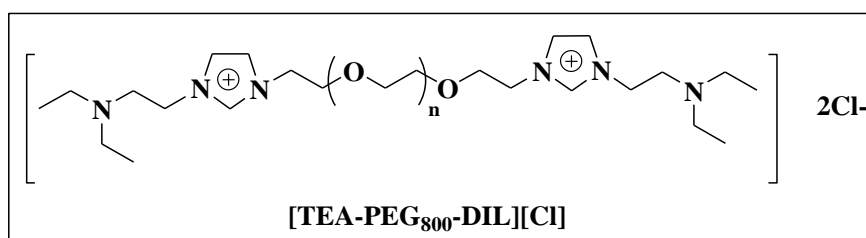
Fig. 5A.7: Structure of [TEA-PEG$_{800}$-DIL][Cl]
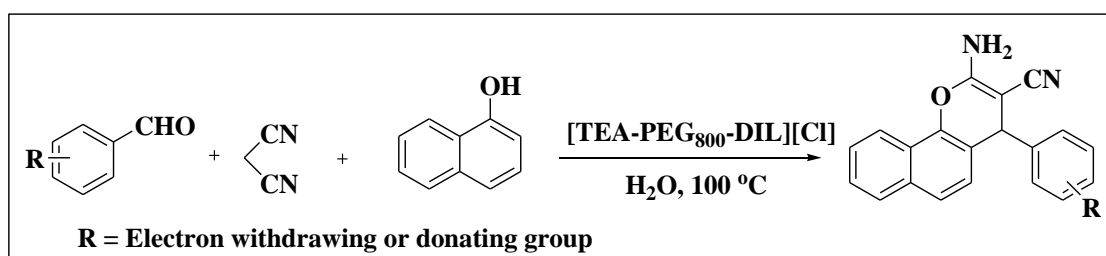
Scheme 5A.25: Synthesis of 2-amino-2-chromene derivatives catalyzed by [TEA-PEG$_{800}$-DIL][Cl]

From the above literature review we observe many useful applications of PEG-based geminal dicationic ILs as efficient reusable solvent/catalyst systems at lower to higher temperature reaction with retention of maximum catalytic activities up to several runs. Most of the PEG-based catalysts could be separated and reused by simple

decantation of reaction mixture solution in PEG-DILs immiscible solvent at different temperature as solvent-dependent biphasic system. Some of the PEG-ILs are Bronsted acidic from the anionic proton and also from presence of N-alkylsulfonic group or N-sulfonic group in the cationic parts. There is only one example of PEG-bridged benzimidazolium -N-SO$_3$H functionalized geminal dicationic IL catalyst [53] and no reports are found with direct -N-SO$_3$H group bearing imidazolium and ammonium based acidic DILs till 2016. These acidic ILs have been utilized in several acid catalyzed multicomponent syntheses of heterocycles, functional group transformations and also for acid catalyzed formation of 5-hydroxymethylfurfural (HMF) from biomass which is very essential chemical intermediate for synthesis of value-added chemical products in the context of sustainable development process.

5A.3. Review of ionic liquid mediated/ catalyzed conversion of biomass to HMF

Biomass is an alternative substitute of fossil fuel which is abundant and widely-distributed in nature to produce liquid fuels and chemical intermediates for the synthesis of chemical product in industry [57-60]. The most common methods of biomass conversions into fuels or fuel precursors are pyrolysis [61] gasification [62] transesterification [63] and hydrolysis [64]. Out of these methods, the control hydrolysis of polysaccharides obtained from raw biomass into selective monosaccharides can form the basis of various chemical processes such as fermentation, selective oxidation, and controlled carbon-carbon bond formation [58, 65-67]. The acid-catalyzed hydrolysis of carbohydrates occur at elevated temperature in water with many side products [68, 69] while the selective enzyme-catalyzed reactions prefer lower temperature due to limited thermal stability of enzymes with a slower rate [70]. The above drawbacks of traditional hydrolysis of carbohydrate led to observation of dissolution and decrystallization of cellulose in 1-butyl-3-methyl imidazolium chloride ionic liquid as reported by Rogers et al. [71] in 2002. Further studies described depolymerization of carbohydrates in ILs as a consequence of disruption of intermolecular H-bonds between different cellulose chains [72, 73].

Retention of more glycosidic bonds in cellulose/hemicelluloses at considerably lower temperature in ILs may be the reason for efficient conversion of carbohydrates to monosaccharides [74-78] and then to other degradation products as compared to mineral

acid-catalyzed hydrolysis processes [68]. It was found in several studies that major amount of degradation products of carbohydrates in [BMIM]Cl in acidic medium are furfural and 5-hydroxy methyl furfural (HMF) along with other side products [68, 75-78]. This 5-hydroxy methyl furfural (HMF) is one of the versatile five-carbon chemical intermediate formed by acid catalyzed dehydration of monosaccharides in ionic liquids which can be converted to many useful chemicals and liquid fuels [79, 80]. All these studies presented somewhat different results regarding the stability of monosaccharides in under acidic conditions.

Then onwards, the ionic liquid mediated/catalyzed conversion of biomass to HMF under controlled route had received major recognition in the domain of ionic liquids fields by dehydration of carbohydrate as sustainable development approach of chemical processes [81-85]. This review section gives a brief discussion of different reports related to conversion of biomass in the form of polysaccharides, cellulose, monosaccharides etc. in to 5-hydroxymethyl furfural (HMF) in ionic liquids as reaction medium or dual solvent-catalyst systems till 2016.

Following the initial reports of Rogers [71], Lansalot-Matras and Moreau observed the degradation of fructose in [BMIM]Cl with Amberlyst-15 as ion-exchanged resin catalyst [86] at 80 °C to get maximum 40-50% yield of HMF during 3 h reaction. The formation of HMF was increased up to 85% yield after addition of toluene as the organic extractor by liquid/liquid extraction process.

The same group utilized 1-H-3-methyl imidazolium chloride [HMIM]Cl as dual task-specific solvent/catalyst in a microbatch reactor at 90 °C to form 92% yield of HMF within 15-45 min from fructose [83].

Yong et al. [82] introduced a NHC/CrCl$_2$ (NHC=N-heterocyclic carbene) complexes (**Fig. 5A.8**) as catalysts for the sugar dehydration reaction in [BMIM]Cl that efficiently convert both fructose and glucose into HMF in good to excellent yields (81-96%) 100 °C .

Sievers et al. [87] studied the stability and reactivity of monosaccharides, furfural, and 5-hydroxymethyl-2-furfural (HMF) in [BMIM]Cl at 120 °C in presence of H$_2$SO$_4$.. They found formation of higher amount of HMF from fructose as compared to mannose, glucose, and xylose even in absence of the acid. The conversion of mannose, glucose and xylose involves more complex mixtures of products (**Scheme 5A.26**). Compared to the monosaccharides, HMF and furfural showed high stabilities in

BMImCl under acidic conditions. One possible pathway shown for HMF was hydrolysis of it to form levulinic acid and formic acid (**Scheme 5A.27**).
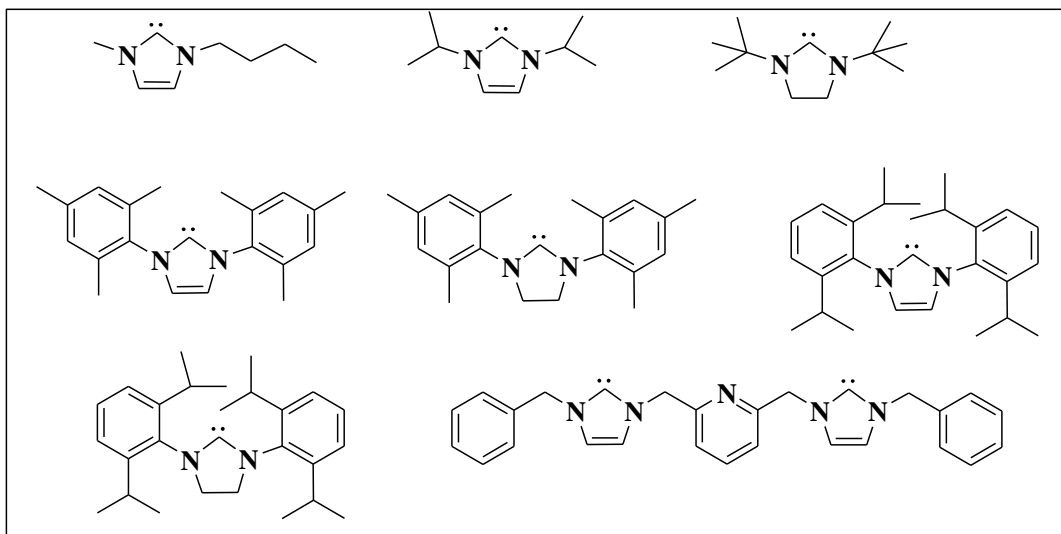
Fig. 5A.8: Structures of NHC used by Yong et al.
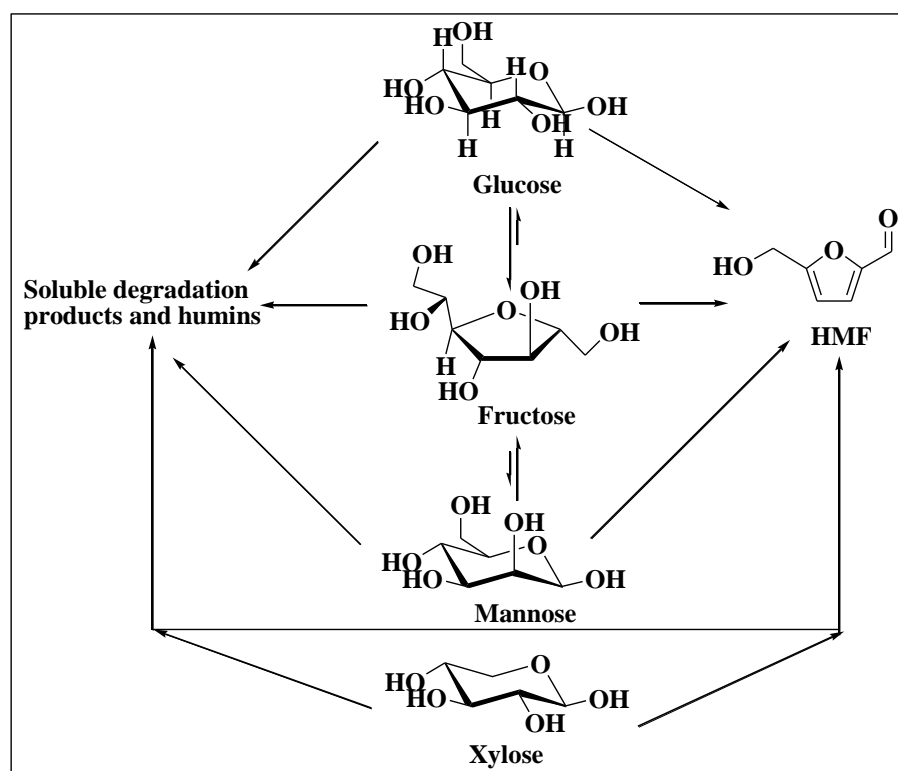
Scheme 5A.26: Possible reaction pathways for the conversion of glucose, fructose and mannose in to HMF and other degradation products
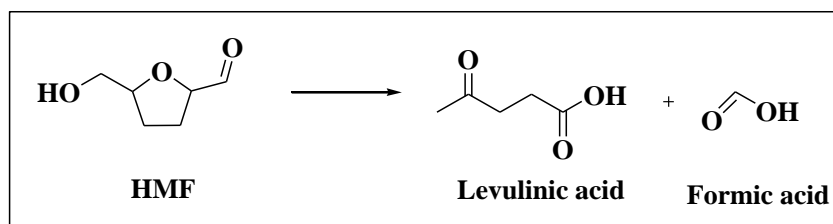
Scheme 5A.27: Hydrolysis of HMF catalyzed in [BMIM]Cl

Ray et al. [88] studied the role of [BMIM]Cl as reaction medium for dehydration of fructose at different temperature using P_2O_5 as catalyst. The acidic nature of P_2O_5 along with its hygroscopic property efficiently promotes the reaction with 81.2% yield at 50 °C in 60 mins.

Wei et al. [89] used $IrCl_3$ and $AuCl_3.HCl$ as catalysts for dehydration of carbohydrates to HMF in ([BMIM]Cl) and triethylaminesulphate ($[Et_3NH][HSO_4]$) (**Fig. 5A.9**). Using 7 mol% of $IrCl_3$ in [BMIM]Cl, 97.7% fructose conversion with 89% HMF selectivity was achieved. The dehydration of other carbohydrates such glucose, sucrose and maltose were found to be rather difficult than fructose.
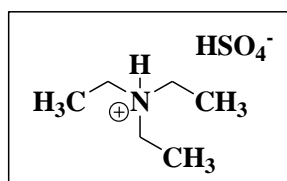
Fig. 5A.9: Structure of $[Et_3NH][HSO_4]$

Jiang et al. [90] studied the hydrolysis of cellulose to glucose and HMF catalyzed by a variety of acidic ionic liquids (**Fig. 5A.10**) in the temperature range of 80-120 °C. The acid strength of the ILs played a crucial role in the breaking of β-1, 4 glycosidic bonds in the cellulose to form glucose, and further convert glucose to HMF.

Hu et al. [91] utilized chromium (III) chloride ($CrCl_3.6H_2O$) and boric acid ($B(OH)_3$) as double catalysts in ([BMIM]Cl) (**Scheme 5A.28**) for conversion of glucose to HMF. Highest HMF yield of 78.8% was obtained at 120 °C within 30 min reaction time. Furthermore, use of tetraethyl ammonium chloride (TEAC) as solvent also enhanced the HMF yield.
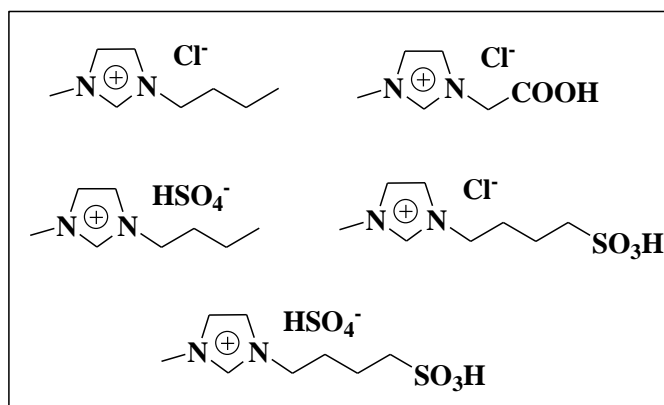
Fig. 5A.10: Structures of acidic ILs used by Jiang et al.
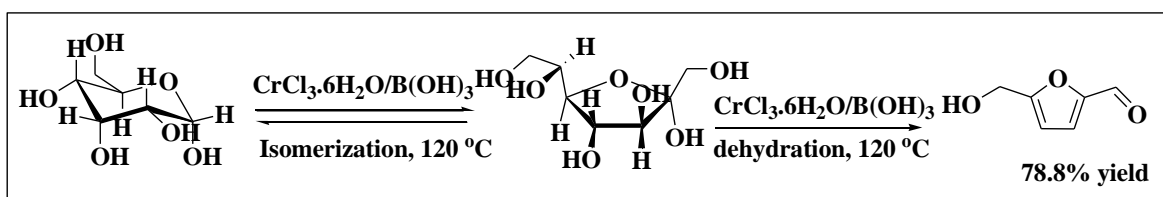
Scheme 5A.28: Conversion of glucose in to HMF in [BMIM]Cl

Hu et al. [92] found 51.9% yield of HMF from glucose using 12-tungstophosphoric acid (12-TPA)/boric acid (B(OH)$_3$) as synergistic catalytic system in ([BMIM]Cl) at 140 °C in 40 min reaction time. After extraction of HMF, the catalyst in IL could be reused for next five consecutive runs with stable activity.

In 2013, Hu et al. [93] observed the catalytic activity of three environmental-benign and low-cost carbon-based solid acid catalysts containing -SO$_3$H, -COOH and phenolic -OH groups for conversion of glucose into 5-hydroxymethylfurfural in ([BMIM]Cl) ionic liquid. Among them, cellulose-derived carbonaceous catalyst (CCC) displayed the best catalytic activity with 46.4% HMF yield at 160 °C within 15 min. This CCC catalyst in [BMIM]Cl was also utilized for conversion of fructose, sucrose, maltose, cellobiose, starch and cellulose into HMF.

The use of microwave energy for the synthesis of HMF from carbohydrate was first investigated by Zhou et al. [94] in ([BMIM]Cl) using ScCl$_3$ as catalyst within short time. A maximum of 73.4% of HMF yield was obtained in 2 mins with the microwave power at 400 W.

The direct formation of HMF from cottonseed hull biomass in [Bmim]Cl/CrCl$_3$·6H$_2$O/HCl catalytic system was carried out by Wang et al. [95]. Under the optimized reaction condition, 51% yield of HMF was obtained at 130 °C for 2h.

The hydrolysis of cellulose into HMF was performed by Xiong et al. [96] in [Bmim]Cl using a core-shell Fe_3O_4@SiO_2-SO_3H acid catalyst. It showed a good activity with RS (reducing sugar) yield of 73.2% at 130 °C after 8 h reaction. The magnetic catalytic system could be easily recovered from the reaction mixture with the help of an external magnet and reused for several times.

In 2015, Zhou et al. [97] devised a ternary biphasic system of glycol dimethyl ether (GDE) as the extraction phase, and [BMIM]Cl/$CrCl_3$/glucose in combination with a partitioned amount of GDE and an appropriate amount of water as the reaction phase for efficient conversion of glucose to 5-HMF in 64.5 mol% yield from a very high glucose concentration (80 wt% with respect to the ionic liquid) at 108 °C. This 5-HMF yield in the [BMIM]Cl–GDE–H_2O ternary biphasic system nearly doubled that obtained in the single [BMIM]Cl/$CrCl_3$/glucose reaction phase.

In 2016, Zhang et al. [98] employed a biphasic system consisted of ([BMIM]Cl) as the solvent, chromium chloride as the catalyst and methyl benzene as the extraction reagent to efficiently convert the microcrystalline cellulose in to the HMF. Under the optimum reaction conditions, 27% and 55% yields of glucose and HMF were obtained respectively. The IL could be successfully reused for two cycles.

Zhou et al. [99] examined the catalytic behavior of chromium exchanged bentonite (bentonite-Cr) in ([BMIM]Cl) and dimethylsulfoxide (DMSO) mixtures in the conversion of glucose into HMF. The authors investigated the effect of various reaction conditions such as catalyst loading, temperature, reaction duration and solvent over the reaction course. The HMF yield of 61.45% was obtained at 120 °C within 4h. After five reaction runs, the catalyst showed about 57.26% yield of HMF.

Nguyen et al. [100] in 2015 synthesized mesoporous poly(vinyl sulfonic-co-divinylbenzene) (VS-DVB) and magnetic polymer (VS-DVB/$CoFe_2O_4$) as solid acids and used them as catalysts in ([BMIM]Cl) for transformation of cellulose into HMF. A combination of VS-DVB/$CoFe_2O_4$ and $CrCl_3$·$6H_2O$ in ionic liquids was employed at optimal condition for cellulose conversion and it improved the HMF yield. The magnetic catalysts were readily separated from the reaction mixture with the help of magnet and reused with little loss in activity.

Shi et al. in [101] utilized catalytic amount of another ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) in N, N-dimethylformamide (DMF) for the

conversion of fructose and glucose into HMF at 100 $^{\circ}$C at different time without any added metal salts or acids which leads to reasonable HMF yields (84.9%) and selectivities.

The catalytic activity of amino acids in 1-ethyl-3-methylimidazolium bromide ([Emim]Br) IL was explored by Su et al. [102] for conversion of sucrose to HMF at different temperature. Among the amino acids, tyrosine displayed the best catalytic activity and under the optimal reaction conditions, 76% yield of HMF was obtained at 160 °C within 4h. The uniquely effective catalytic activity of tyrosine could be attributed to two types of active sites in tyrosine: free base NH_2 and dissociated H^+ sites.

The same [EMIM]Br IL was also used by Xu et al. [103] as reaction medium for conversion of glucose to HMF using tin containing molecular sieves (Sn-MCM-41) as bifunctional heterogeneous catalyst A maximum of 70% conversion was achieved using this catalyst at 110 °C after 4h. The same catalytic system was also able to convert the fructose in to HMF more efficiently.

Yi et al. [104] (**Fig. 5A.11**) utilized 1-octyl-3-methylimidazolium chloride IL as medium to scrutinize the catalytic action of chromium fluoride (CrF_3) for conversion of raw tapioca root biomass with high starch into HMF. The yield of HMF was significantly dependent on the concentration of CrF_3 catalyst. The highest yield (52.6±4.8 wt %) was obtained at 1% CrF_3, but over 1% CrF_3 yield began to decline. The combined addition of CrF_3 and $CrBr_3$ in the reaction mixture showed 1.3-fold higher yield than CrF_3 alone.
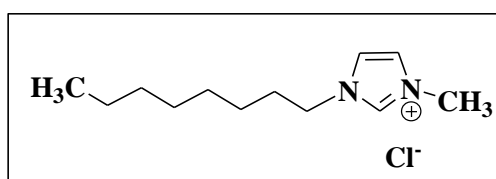
Fig. 5A.11: Structure of 1-octyl-3-methylimidazolium chloride IL

Kuo et al. [105] investigated hydrothermally treated mesoporous titania (HT-MTN) and zirconia nanoparticles (HT-MZrN) as catalysts in 1-ethyl-3-methylimidazolium chloride, [EMIM]Cl) for the conversion of cellulose to glucose and 5-hydroxymethylfurfural (HMF). In this study we observed 18.2% and 29.2% yields of

HMF for the HT-MTN and HT-MZrN catalysts respectively at 120 °C with the optimized amount of catalyst.

Zhang et al. [106] synthesized two acid-chromic chloride functionalized catalysts (ATP–SO$_3$H-Cr(III) and HNTs–SO$_3$H–Cr(III)) by grafting -SO$_3$H and Cr(III) onto the surface of treated attapulgite (ATP) and halloysite nanotubes (HNTs). Their catalytic activities were evaluated for one-pot conversion of cellulose to 5-hydroxymethylfurfural (HMF) in ([EMIM]-Cl) IL which displayed HNTs–SO$_3$H–Cr(III) as the best catalyst with a yield of 41.22% under the optimal conditions.

Bao et al. [83] utilized Brønsted acidic ionic liquid 3-allyl-1-(4-sulfobutyl)imidazolium trifluoromethanesulfonate, as well as its Lewis acid derivative, 3-allyl-1-(4-sulfurylchloride butyl)imidazolium trifluoromethanesulfonate, for dehydration of fructose in DMSO under microwave irradiation (**Scheme 5A.29**). It was concluded that the type of acidic ionic liquid used played a significant role in the reaction, and the Lewis acidic ionic liquid acts more effectively than its Brønsted acidic counterpart.
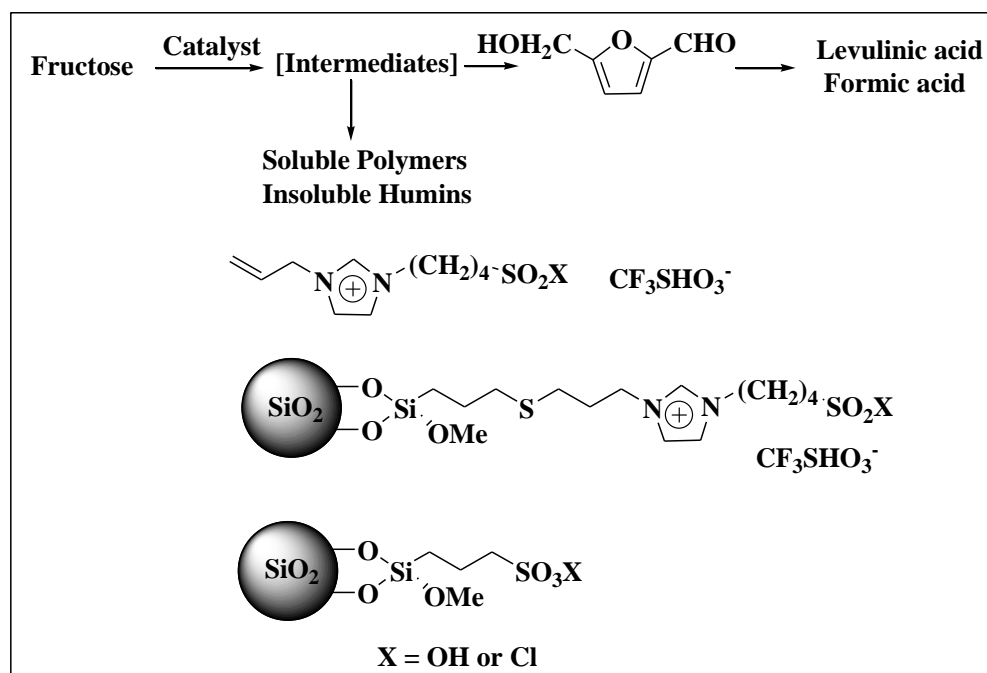
Scheme 5A.29: Dehydration of fructose in to HMF catalyzed by acidic catalysts

Tao et al. [107] devised another acidic IL 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate IL as catalyst in water-4-methyl-2-pentanone (MIBK) biphasic system for dehydration of fructose to HMF. The authors have

achieved high fructose conversion of 100% with HMF yield of 94.6% at 120 °C for 180 min reaction time in water-4-methyl-2-pentanone (MIBK) biphasic system. The selectivity decreased with increasing temperature and reaction time. The IL was recycled for six consecutive runs.

Tao et al. [108] developed a route for dehydration of D-glucose in to HMF using -SO$_3$H functionalized acidic ILs as catalysts (**Fig. 5A.12**) and H$_2$O-4-methyl-2-pentanone (MIBK) biphasic system as solvent under mild conditions. Within 360 min reaction time, 97.4% glucose conversion was achieved with 75.1% HMF selectivity at 120 °C. High reaction temperature, prolonged reaction time and water content in the system had a negative impact on the reaction course. The IL could be successfully recycled for five consecutive runs with the same catalytic activity.

IL-1: R = CH$_3$; X$^-$ = CF$_3$COO$^-$ **IL-2: R = CH$_3$; X$^-$ = CH$_3$COO$^-$**

IL-3: R = CH$_3$; X$^-$ = H$_2$PO$_4^-$ **IL-4; R = CH$_3$; X- = *p*-CH$_3$C$_6$H$_4$SO$_3^-$**

IL-5: R = CH$_3$; X$^-$ = CF$_3$SO$_3^-$ **IL-6: R = CH$_3$, X$^-$ = HSO$_4^-$**

IL-7: R = (CH$_2$=CH); X$^-$ = HSO$_4^-$ IL-8: R = *n*-C$_4$H$_9$, X$^-$ = HSO$_4^-$
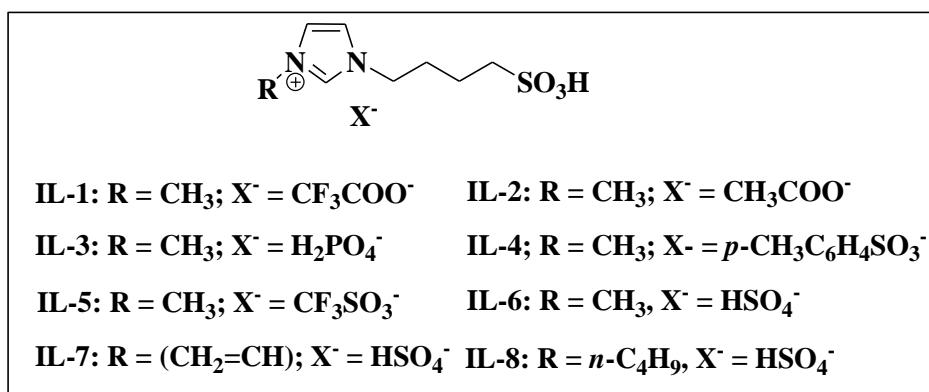
Fig. 5A.12: Structure of -SO$_3$H functionalized IL prepared by Tao et al.

Tong et al. [109] utilized catalytic amount of 1-methylimidazolium-based and N-methylmorpholinium-based ionic liquids (**Scheme 5A.30**) for the synthesis of HMF from D-fructose and sucrose. The use of N-methylmorpholinium methyl sulfonate ([NMM]$^+$[CH$_3$SO$_3$]$^-$) catalyst in DMF-LiBr medium produced 74.8% and 47.5% yields of HMF from D-fructose and sucrose respectively at 90 °C for 2h. Tong also carried out this work using the same of series of IL in DMSO [110]. In this case, 72.3% yield of HMF with 87.2% selectivity was obtained in presence of 7.5 mol% of [NMP]$^+$[CH$_3$SO$_3$]$^-$ under the same reaction condition.
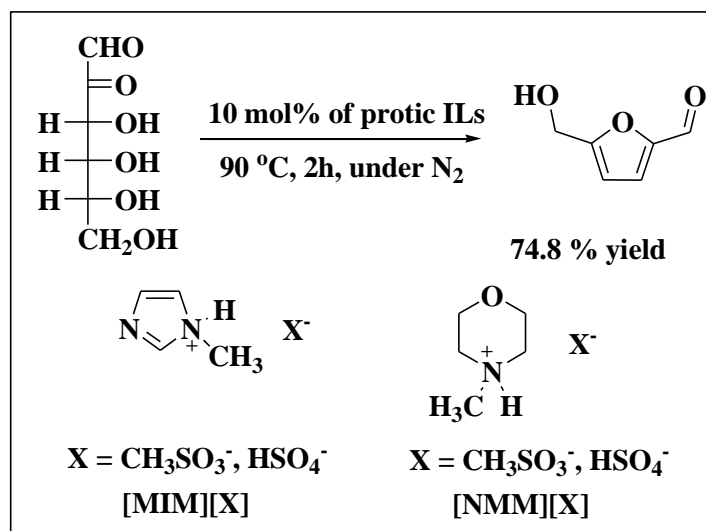
Scheme 5A.30: Dehydration of D-fructose catalyzed by protic ILs

Zhou et al. [111] prepared metal salt containing acidic bifunctional ionic liquids Cr([PSMIM]HSO$_4$)$_3$, CuCr([PSMIM]SO$_4$)$_5$ from the reactions of 1-(3-sulfonic acid)propane-3-methylimidazole hydrosulfate ([PSMIM]HSO$_4$) with CrCl$_3$ or CrCl$_3$-CuCl$_2$ in different molar ratios to investigate degradation of microcrystalline cellulose in [BMIM]Cl ionic liquid at atmospheric pressure. The effect of various parameters such as reaction temperature, amount of catalysts, reaction time, ionic liquid purity and cellulose concentration on conversion were investigated. The HMF yield of 53% and TRS (total reducing sugar) yield of 94% were achieved at 120 °C in [BMIM]Cl within 5 h with 0.05 g Cr([PSMIM]HSO$_4$)$_3$/2.0 g [BMIM]Cl catalytic system.

Ding et al. [112] studied different acidic ILs catalyzed conversion of microcrystalline cellulose (MCC) to HMF and metal salts as co-catalyst in 1-ethyl-3-methylimidazolium acetate ([emim][Ac]) as ionic liquid solvent (**Fig. 5A.13**). The combination of CuCl$_2$ in 1-(4-sulfonic acid) butyl-3-methylimidazoliummethyl sulfate ([C$_4$SO$_3$Hmim][CH$_3$SO$_3$]) was found to be the most efficient catalyst with 69.7% yield of HMF.

Shi et al. [113] in a report described the use of polypropylene fiber supported ILs (**Fig. 5A.14**) as catalysts for the dehydration of fructose. Using DMSO as the reaction medium, 86.2% yield of HMF was obtained within 30 min, while in mixed aqueous system, 84.7% yield of HMF was obtained within 45 min at 100 °C. The formed HMF could be easily extracted via distillation and the catalytic system could be recycled for next tenth runs.
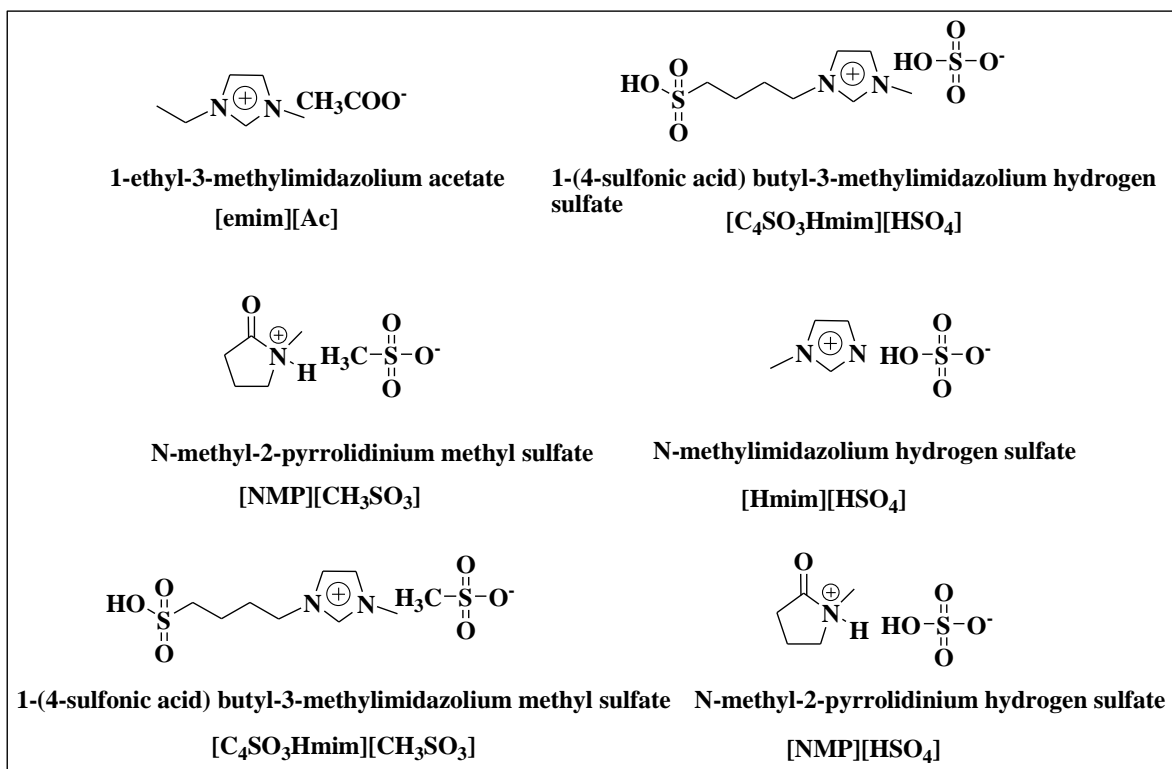
Fig. 5A.13: Structures of ILs used by Ding et al.
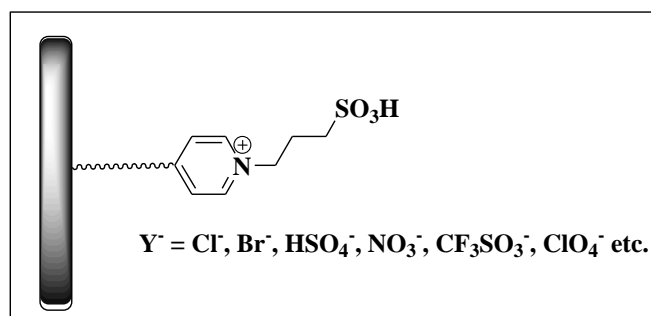
Fig. 5A.14: Polypropylene fiber supported ILs prepared by Shi et al.

A thermos-regulated recyclable Brønsted acidic ionic liquid catalyst [HO$_2$CMMIm]Cl (**Fig. 5A.15**) was developed by Ma et al. [114] in isopropanol for the dehydration of fructose into HMF. Under the optimized reaction temperature 110 $^{\circ}$C, 91.2 mol% yield of HMF was obtained with 100% conversion of fructose in 3 h. The precipitation of ionic liquid was observed at low temperature from the solvent and it could be reused for next sixth cycles after decantation of the solvent in each run.
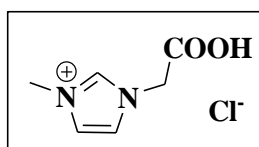
Fig. 5A.15: Structure of [HO$_2$CMMIm]Cl

Ramli and Amin [115] examined the catalytic efficiency of three acidic functionalized ILs: [BMIM][FeCl$_4$], [SMIM][Cl] and [SMIM][FeCl$_4$] (**Fig. 5A.16**) in the conversion of glucose in to HMF and levulinic acid (LA). Among the tested ILs, [SMIM][FeCl$_4$] exhibited the best catalytic activity. The yields of 5-HMF and LA obtained were 18% and 68%, respectively after 4 h at 150 °C.
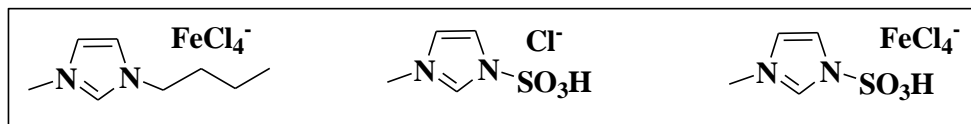
Fig. 5A.16: Structure of [BMIM][FeCl$_4$], [SMIM][Cl] and [SMIM][FeCl$_4$]

Huang et al. [116] carried out the dehydration of sugars using caprolactam hydrogen sulfate ([CPL]HSO$_4$) (**Fig. 5A.17**) ionic liquid as the catalyst and metal halide as the co-catalyst in water/proprylene glycol monomethyl ether solvent system. Under the optimum conditions, 80.5% yield of HMF was obtained at 105 °C within 90 min. 70% yield of HMF was obtained using the catalyst after being used for five runs.
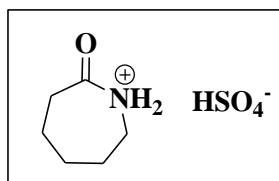
Fig. 5A.17: Structure of [CPL]HSO$_4$

Yang et al. [117] also studied the effect of different ionic liquids, viz., N-methyl-2-pyrrolidone hydrogen sulfate ([NMP]HSO$_4$), N-methyl-2-pyrrolidone methyl sulfate ([NMP]CH$_3$SO$_3$), N-methyl-2-pyrrolidone chlorine ([NMP]Cl) and N-methyl-2-pyrrolidonebromide ([NMP]Br) (**Fig. 5A.18**) in the conversion of glucose into HMF in N, N-dimethylacetamide (DMA) over AlCl$_3$. Among them, ([NMP]Br) exhibited the highest catalytic activity with 57% yield of HMF under mild conditions.

Hu et al. [118] performed the one pot efficient conversion of inulin into HMF using two ionic liquids: choline chloride (ChoCl)/oxalic acid and ChoCl/citric acid as solvent/catalyst systems at relatively lower temperature (**Scheme 5A.31**). The ionic liquids could be reused after simple separation.
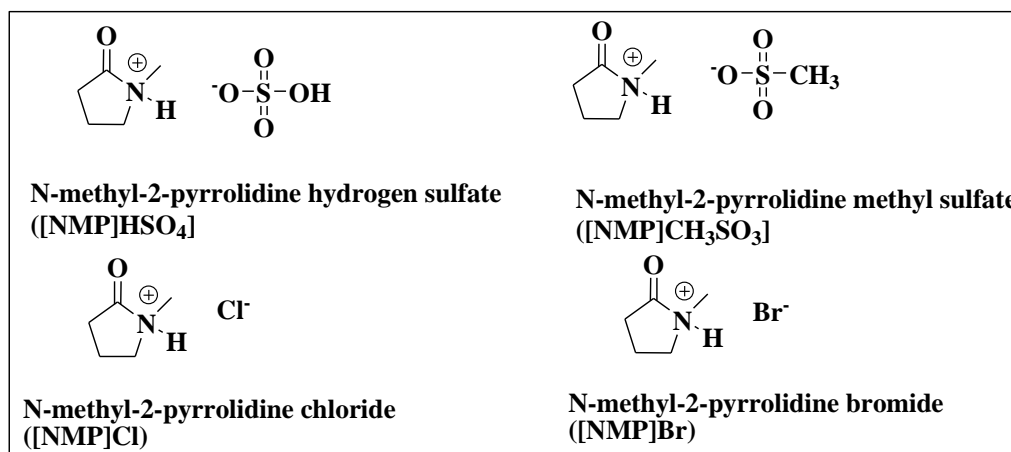
Fig. 5A.18: Structures of ILs prepared by Yang et al.
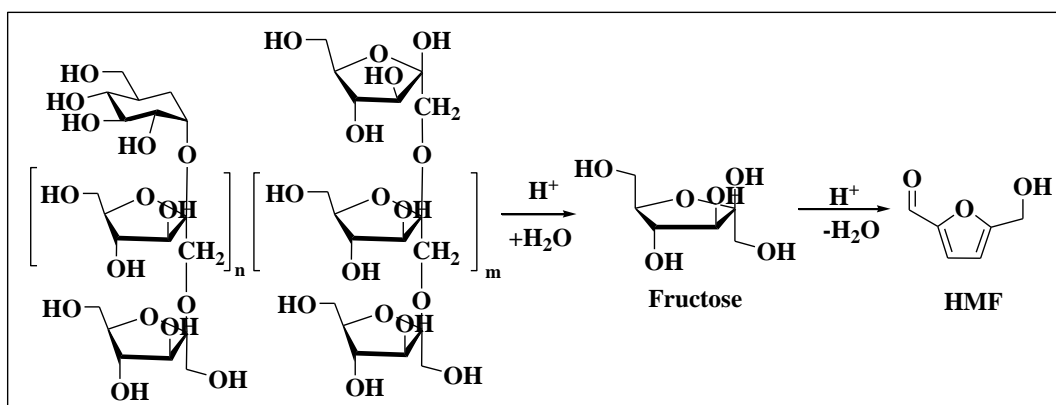
Scheme 5A.31: Conversion of insulin in to HMF

Hu et al. [119] in the same year reported SnCl$_4$ catalyst in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMim]BF$_4$) for the dehydration of glucose into HMF. This catalytic system proved to be an efficient one also in case of fructose, sucrose, cellobiose, insulin and starch feed stocks. Probable formation of five-membered-ring chelate complex of Sn and glucose might play the key role for the formation of HMF.

Jadhav et al. [120] also utilized short oligo ethylene glycol bridged dicationic ILs (**Fig. 5A.19**) as catalyst for selective dehydration of fructose and glucose into HMF. The use of one equivalent of dicationic ionic liquid, [TetraEG(mim)$_2$][OMs]$_2$ produced 92.3% of HMF for fructose at 120 °C within 40 min while 67.2% of HMF was obtained from sucrose at 120 °C in 150 min using two equivalents of the same dicationic IL (**Scheme 5A.32**). The same IL catalyst gave 100% conversion of fructose and sucrose

with 81.2% and 62.2% of HMF yields respectively after addition of NiCl$_2$.6H$_2$O as a co-catalyst at 100 °C. These dicationic ILs could be recycled for next five cycles with significant activity.
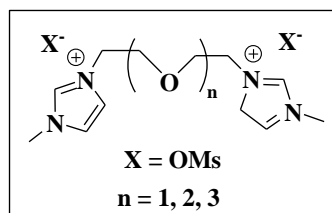
Fig. 5A.19: Structure of ILs prepared by Jadhav et al.
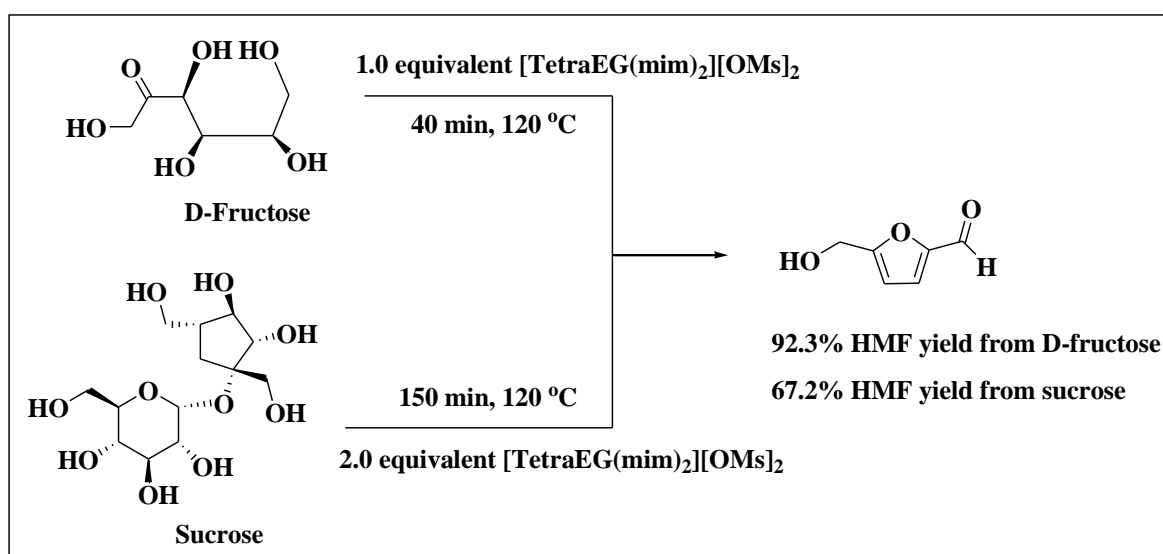
Scheme 5A.32: Dehydration of fructose and sucrose with dicationic RTILs

Qu et al. [121] studied the conversion and kinetic aspects of fructose and glucose to HMF using 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ([C$_2$OHMIM]BF$_4$) IL as catalyst cum solvent. In case of glucose, the yield of HMF was as high as 67.3% after 1 h at 180 °C in DMSO. The catalyst was separated from the reaction mixture by simply distilling the solvent and reused for six times.

Qu et al. [122] also utilized basic IL 1-butyl-3-methylimidazolium hydroxide ([BMIM]OH) as catalyst in DMSO for dehydration of carbohydrates into 5-hydroxymethylfurfural in thermal treatment. The HMF was obtained with 91.6% yield from a mass ratio of IL and fructose of 0.5 at 160 °C. The effects of varying the solvent, IL concentration, temperature, and reaction time on the reaction were studied in detail.

Walia et al. [123] examined silica supported boric acid as heterogeneous catalyst for conversion of mono- and polysaccharides to 5-hydroxymethylfurfural in [bmim]HSO$_4$, [1, 3-dimim]HCO$_3$ and [bmim]BF$_4$ ionic liquid under mild condition. Fructose, glucose, sucrose, inulin, and cellulose were successfully converted to HMF with this catalytic system in moderate to excellent conversion. The catalyst and the solvent system were easily recycled for four cycles without obvious loss in activity.

Song et al. [124] studied the conversion of cellobiose into HMF using poly ionic liquid ([IMEP]BF$_4$) as catalyst. The poly ionic liquid was developed from imidazolium and epichlorohydrin (**Scheme 5A.33**). Using 0.25g of this poly ionic liquid against 0.5g of cellobiose in DMSO at 180 °C, the authors obtained 39.2% yield of HMF in 420 min.
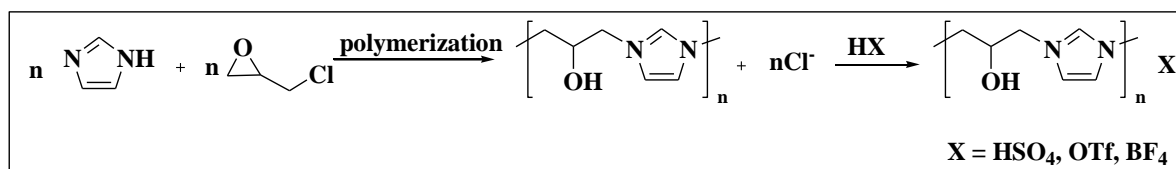
Scheme 5A.33: Conversion of cellobiose into HMF catalyzed by [IMEP]BF$_4$

Qu et al. [125] investigated several acidic and basic IL catalysts (**Fig. 5A.20**) in the production of 5-HMF from disaccharide with variation of different factors including reaction temperature, IL dosage, solvent and reaction time. Out of these screened ILs, 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ([AEMIM]BF$_4$) showed the highest catalytic activity and selectivity. With this catalytic system, 68.71% and 24.73% yield of HMF was obtained from sucrose and cellobiose respectively at 160 °C in 6 h.

From the above literature review, we have observed the efficient utility of different PEG based DILs in the synthesis of HMF from biomass resources. As already mentioned in the previous section, there was no report related to N-SO$_3$H functionalized 2-imidazolium and ammonium based DILs till 2016. In this regard, we decided to prepare eight new members of two types of PEG6000 linked dicationic ionic liquids (DILs) with 2-methylimidazole and diphenylamine as cations and trifluroacetate, trichloroacetate, acetate and hydrogen sulfate as different anions. The catalytic activities of these DILs were explored for the efficient conversion of fructose in to HMF in different organic solvents under reflux condition.
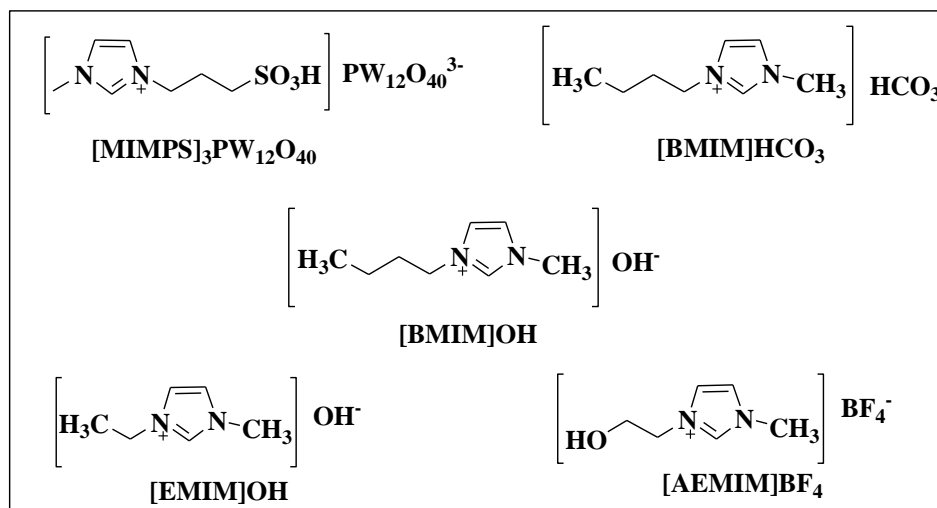
Fig. 5A.20: Structures of ILs used by Qu et al.

References

1. Anderson, J. L., Ding, R., Ellern, A., and Armstrong, D.W. Structure and properties of high stability geminal dicationic ionic liquids. *Journal of the American Chemical Society*, 127(2):593-604, 2005.

2. Han, X. and Armstrong, D. W. Using geminal dicationic ionic liquids as solvents for high-temperature organic reactions. *Organic letters*, 7(19):4205-4208, 2005.

3. Xiao, J. C. and Shreeve, J. N. M. Synthesis of 2, 2 'biimidazolium-based ionic liquids: Use as a new reaction medium and ligand for palladium-catalyzed suzuki cross-coupling reactions. *The Journal of Organic Chemistry*, 70(8):3072-3078, 2005.

4. Wang, R., Jin, C. M., Twamley, B., and Shreeve, J. N. M. Syntheses and characterization of unsymmetric dicationic salts incorporating imidazolium and triazolium functionalities. *Inorganic Chemistry*, 45(16):6396-6403, 2006.

5. Jin, C. M., Ye, C., Phillips, B. S., Zabinski, J. S., Liu, X., Liu, W., and Jean'ne, M. S. Polyethylene glycol functionalized dicationic ionic liquids with alkyl or polyfluoroalkyl substituents as high temperature lubricants. *Journal of Materials Chemistry*, 16(16):1529-1535, 2006.

6. Anderson, J. L. and Armstrong, D. W. Immobilized ionic liquids as high-selectivity/high-temperature/high-stability gas chromatography stationary phases. *Analytical Chemistry*, 77(19):6453-6462, 2005.

7. Anderson, J. L., Armstrong, D. W., and Wei, G. T. Ionic liquids in analytical chemistry. *Analytical Chemistry*, 78:2893–2902, 2006.

8. Lambertus, G. R.; Crank, J. A.; McGuigan, M. E.; Kendler, S.; Armstrong, D. W., and Sacks, R. D. *Journal of Chromatography A*, 1135:230-240, 2006,

9. Huddleston, J. G., Willauer, H. D., Swatloski, R. P., Visser, A. E., and Rogers, R. D. Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction. *Chemical Communications*, (16):1765-1766, 1998.

10. Visser, A. E., Holbrey, J. D., and Rogers, R. D. Hydrophobic ionic liquids incorporating N-alkylisoquinolinium cations and their utilization in liquid–liquid separations. *Chemical Communications*, (23):2484-2485, 2001.

11. Armstrong, D. W., Zhang, L. K., He, L., and Gross, M. L. Ionic liquids as matrixes for matrix-assisted laser desorption/ionization mass spectrometry. *Analytical Chemistry*, 73(15):3679-3686. 2001.

12. Carda-Broch, S., Berthod, A., and Armstrong, D. W. Ionic matrices for matrix-assisted laser desorption/ionization time-of-flight detection of DNA oligomers. *Rapid Communications in Mass Spectrometry*, 17(6):553-560, 2003.

13. Soukup-Hein, R. J., Remsburg, J. W., Dasgupta, P. K., and Armstrong, D. W. A general, positive ion mode ESI-MS approach for the analysis of singly charged inorganic and organic anions using a dicationic reagent. *Analytical Chemistry*, 79(19):7346-7352, 2007.

14. Benaglia, M., Puglisi, A. and Cozzi, F. Polymer-supported organic catalysts. *Chemical Reviews*, 103(9):3401-3430, 2003.

15. Wu, F. W., Hou, R. S., Wang, H. M., Kang, I. J., and Chen, L. C. Catalyst free indirect Friedländer synthesis of substituted quinolines from alcohols in PEG-400. *Journal of the Chinese Chemical Society*, 59(4):535-539, 2012.

16. Tang, S., Baker, G. A., and Zhao, H. Ether-and alcohol-functionalized task-specific ionic liquids: attractive properties and applications. *Chemical Society Reviews*, 41(10):4030-4066, 2012.

17. Zhao, Y. N., Yang, Z. Z., Luo, S. H., and He, L. N. Design of task-specific ionic liquids for catalytic conversion of CO_2 with aziridines under mild conditions. *Catalysis Today*, 200:2-8, 2013.

18. Hu, Y. L., Wang, P. C., Chen, T., and Lu, M. Facile and efficient amination of organic halides catalyzed by copper sulfate in PEG 1000-

DIL/methylcyclohexane temperature-dependent biphasic system. *Journal of the Chinese Chemical Society*, 57(4A):604-611, 2010.

19. Ren, Y. M. and Cai, C. A green procedure for the protection of carbonyl compounds catalyzed by iodine in ionic liquid. *Tetrahedron Letters*, 49(50):7110-7112, 2008.

20. Ren, Y. and Cai, C. Molecular iodine in ionic liquid: a green catalytic system for esterification and transesterification. *Synthetic Communications,* 40(11):1670-1676, 2010.

21. Ren, Y. M., Shao, J. J., Wu, Z. C., Yang, R. C., Zhang, Z., and Tao, T. X. PEG-1000 based dicationic acidic ionic liquid as an efficient catalyst for Mannich-type reaction in water. *Synthetic Communications*, 44(17):2529-2534, 2014.

22. Ren, Y. M., Shao, J. J., Wu, Z. C., and Xu, M. D. PEG1000-based dicationic acidic ionic liquid catalyzed one-pot synthesis of 1, 4-dihydropyridines via the Hantzsch reaction. *Organic Preparations and Procedures International*, 46(6):545-550, 2014.

23. Ren, Y. M., Shao, J. J., Wu, Z. C., Zhang, S., and Tao, T. X. Facile protection of carbonyl compounds as oxathiolanes and thioacetals promoted by PEG 1000-based dicationic acidic ionic liquid as chemoselective and recyclable catalyst. *Journal of Molecular Liquids*, 196:392-394, 2014.

24. Fang, D., Yang, J., and Jiao, C. Thermal-regulated PEG 1000-based ionic liquid/PM for one-pot three-component synthesis of 2, 4, 5-trisubstituted imidazoles. *Catalysis Science & Technology*, 1(2):243-245, 2011.

25. Hu, Y. L., Jiang, H., Zhu, J., and Lu, M. Facile and efficient hydrolysis of organic halides, epoxides, and esters with water catalyzed by ferric sulfate in a PEG 1000-DAIL [BF$_4$]/toluene temperature-dependent biphasic system. *New Journal of Chemistry*, 35(2):292-298, 2011.

26. Lu, H., Sun, L., Wu, D., Gao, Y., Shi, Y., and Xue, Q. Synthesis of 6-amino-purine derivatives catalyzed by polyethylene glycol 1000-dicationic acidic ionic liquid. *Chinese Journal of Organic Chemistry*, 32(10):1880-1887, 2012.

27. Wang, Y., Zhi, H., and Luo, J. A facile and efficient protocol for esterification and acetalization in a PEG 1000-DAIL/toluene thermoregulated catalyst–media combined systems. *Journal of Molecular Catalysis A: Chemical*, 379:46-52, 2013.

28. Zhao, H., Baker, G. A., Song, Z., Olubajo, O., Crittle, T., and Peters, D. Designing enzyme-compatible ionic liquids that can dissolve carbohydrates. *Green Chemistry*, 10(6):696-705, 2008.

29. Wallert, S., Drauz, K., Grayson, I., Gröger, H., de Maria, P. D., and Bolm, C. Ionic liquids as additives in the pig liver esterase (PLE) catalysed synthesis of chiral disubstituted malonates. *Green Chemistry*, 7(8):602-605, 2005.

30. Holbrey, J. D., Visser, A. E., Spear, S. K., Reichert, W.M., Swatloski, R.P., Broker, G.A., and Rogers, R.D. Mercury (II) partitioning from aqueous solutions with a new, hydrophobic ethylene-glycol functionalized bis-imidazolium ionic liquid. *Green Chemistry*, 5(2):129-135, 2003.

31. Dorjnamjin, D., Ariunaa, M., and Shim, Y. K. Synthesis of silver nanoparticles using hydroxyl functionalized ionic liquids and their antimicrobial activity. *International Journal of Molecular Sciences*, 9(5):807-820, 2008.

32. Zeng, Z., Phillips, B. S., Xiao, J. C., and Shreeve, J. N. M. Polyfluoroalkyl, polyethylene glycol, 1, 4-bismethylenebenzene, or 1, 4-bismethylene-2, 3, 5, 6-tetrafluorobenzene bridged functionalized dicationic ionic liquids: synthesis and properties as high temperature lubricants. *Chemistry of Materials*, 20(8):2719-2726, 2008.

33. Huang, K., Han, X., Zhang, X., and Armstrong, D. W. PEG-linked geminal dicationic ionic liquids as selective, high-stability gas chromatographic stationary phases. *Analytical and Bioanalytical Chemistry*, 389(7-8):2265-2275, 2007.

34. Liu, W.T., Wang, Y.F., Li, W., Yang, Y., Wang, N.N., Song, Z.X., Xia, X.F. and Wang, H.J., 2015. Polyethylene glycol-400-functionalized dicationic acidic ionic liquids for highly efficient conversion of fructose into 5-hydroxymethylfurfural. *Catalysis Letters*, 145(4), pp.1080-1088.

35. Fei, Z., Ang, W. H., Zhao, D., Scopelliti, R., Zvereva, E. E., Katsyuba, S. A., and Dyson, P. J. Revisiting ether-derivatized imidazolium-based ionic liquids. *The Journal of Physical Chemistry B*, 111(34):10095-10108, 2007.

36. In-Whan, K. I. M., Jang, M. D., Ryu, Y. K., Cho, E. H., Lee, Y. K., and Park, J. H. Dipolarity, hydrogen-bond basicity and hydrogen-bond acidity of aqueous poly(ethylene glycol) solutions. *Analytical Sciences*, 18(12):1357-1360, 2002.

37. Döbbelin, M., Azcune, I., Bedu, M., Ruiz de Luzuriaga, A., Genua, A., Jovanovski, V., Cabañero, G., and Odriozola, I. Synthesis of pyrrolidinium-based poly (ionic liquid) electrolytes with poly(ethylene glycol) side chains. *Chemistry of Materials*, 24(9):1583-1590, 2012.

38. Asai, H., Fujii, K., Ueki, T., Sakai, T., Chung, U. I., Watanabe, M., Han, Y. S., Kim, T. H., and Shibayama, M. Structural analysis of high performance ion-gel comprising tetra-PEG network. *Macromolecules*, 45(9):3902-3909, 2012.

39. Klingshirn, M. A., Spear, S. K., Subramanian, R., Holbrey, J. D., Huddleston, J. G., and Rogers, R. D. Gelation of ionic liquids using a cross-linked poly(ethylene glycol) gel matrix. *Chemistry of Materials*, 16(16):3091-3097, 2004.

40. Zhi, H., Lü, C., Zhang, Q., and Luo, J. A new PEG 1000-based dicationic ionic liquid exhibiting temperature-dependent phase behavior with toluene and its application in one-pot synthesis of benzopyrans. *Chemical Communications*, (20):2878-2880, 2009.

41. Luo, J. and Zhang, Q. A one-pot multicomponent reaction for synthesis of 1-amidoalkyl-2-naphthols catalyzed by PEG-based dicationic acidic ionic liquids under solvent-free conditions. *Monatshefte für Chemie-Chemical Monthly*, 142(9):923-930, 2011.

42. Lu, T., Zhang, L., Ge, Z., Ji, Y., and Lu, M. Manganese dioxide and N, N′, N ″-trihydroxyisocyanuric acid: a novel and recyclable catalytic system for aerobic oxidation of toluene derivatives in PEG-1000-based dicationic acidic ionic liquid. *Applied Organometallic Chemistry*, 5(29):276-279, 2015.

43. Luo, J., Xin, T., and Wang, Y. A PEG bridged tertiary amine functionalized ionic liquid exhibiting thermoregulated reversible biphasic behavior with cyclohexane/isopropanol: synthesis and application in Knoevenagel condensation. *New Journal of Chemistry*, 37(2):269-273, 2013.

44. Luo, J., Xing, T. T., Wang, Y. L., and Ju, J. F. An efficient one-pot four-Component Hantzsch reaction to prepare Hydroquinolines catalyzed by a poly(ethylene glycol) bridged dicationic basic ionic liquid under solvent-free conditions. In *Advanced Materials Research*, 781:247-252, 2013.

45. Wang, Y. L., Luo, J., and Liu, Z. L. 8-Hydroxyquinoline functionalized PEG-1000 bridged dicationic ionic liquid as a novel ligand for copper-catalyzed N-

Arylation of imidazoles. *Journal of the Chinese Chemical Society*, 60(8):1007-1013, 2013.

46. Wang, Y., Luo, J., Hou, T., and Liu, Z. Synthesis of a novel diol-functionalized poly(ethylene glycol)-bridged dicationic ionic liquid and its application in copper-catalyzed amination of aryl halides. *Australian Journal of Chemistry*, 66(5):586-593, 2013.

47. Wang, Y. L., Li, Z., Luo, J., and Liu, Z. L. One-pot synthesis of tetrahydrobenzo [b] pyrans catalyzed by PEG-1000 bridged primary amine functionalized dicationic Ionic Liquid in Water. *Journal of the Chinese Chemical Society*, 60(12):1431-1436, 2013.

48. Wang, Y., Luo, J., and Liu, Z. Salicylaldoxime-functionalized poly(ethylene glycol)-bridged dicationic ionic liquid ([salox-PEG1000-DIL][BF$_4$]) as a novel ligand for palladium-catalyzed Suzuki–Miyaura reaction in water. *Applied Organometallic Chemistry*, 27:601-605, 2013.

49. Jadhav, A. H., Chinnappan, A., Patil, R. H., Kostjuk, S.V., and Kim, H. Green chemical conversion of fructose into 5-hydroxymethylfurfural (HMF) using unsymmetrical dicationic ionic liquids under mild reaction condition. *Chemical Engineering Journal*, 243:92-98, 2014.

50. Godajdar, B. M. and Ansari, B. Preparation of novel magnetic dicationic ionic liquid polymeric phase transfer catalyst and their application in nucleophilic substitution reactions of benzyl halides in water. *Journal of Molecular Liquids*, 202:34-39, 2015.

51. Godajdar, B. M. and Mombeni, S. Polyethylene glycol functionalized magnetic dicationic ionic liquids as a novel catalyst and their application in ring opening of epoxides in water. *Journal of the Chinese Chemical Society*, 62(5):404-411, 2015.

52. Liu, W., Wang, Y., Li, W., Yang, Y., Wang, N., Song, Z., Xia, X. F., and Wang, H. Polyethylene glycol-400-functionalized dicationic acidic ionic liquids for highly efficient conversion of fructose into 5-hydroxymethylfurfural. *Catalysis Letters*, 145(4):1080-1088, 2015.

53. Eshghi, H., Mirzaei, M., Hasanpour, M., and Mokaber-Esfahani, M. Benzimidazolium dicationic ionic liquid as an efficient and reusable catalyst for the synthesis of α-aminophosphonates and bis(α-aminophosphonates) under

solvent-free condition. *Phosphorus, Sulfur, and Silicon and the Related Elements*, 190(10):1606-1620, 2015.

54. Jadhav, A. H., Lee, K., Koo, S., and Seo, J. G. Esterification of carboxylic acids with alkyl halides using imidazolium based dicationic ionic liquids containing bis-trifluoromethane sulfonimide anions at room temperature. *RSC Advances*, 5(33):26197-26208, 2015.

55. Jadhav, V. H., Kim, J. G., Jeong, H. J., and Kim, D. W. Nucleophilic hydroxylation in water media promoted by a hexa-ethylene glycol-bridged dicationic ionic liquid. *The Journal of Organic Chemistry*, 80(14):7275-7280, 2015.

56. Wang, Y., Yue, C., Li, X., and Luo, J. Synthesis of a novel poly (ethylene glycol) grafted triethylamine functionalized dicationic ionic liquid and its application in one-pot synthesis of 2-amino-2-chromene derivatives in water. *Comptes Rendus Chimie*, 19(8):1021-1026, 2016.

57. Stöcker, M. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition*, 47(48):9200-9211, 2008.

58. Corma, A., Iborra, S., and Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews*, 107(6):2411-2502, 2007.

59. Chheda, J. N., Huber, G. W., and Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angewandte Chemie International Edition*, 46(38):7164-7183, 2007.

60. Huber, G. W., Chheda, J. N., Barrett, C. J., and Dumesic, J. A. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science*, 308(5727):1446-1450, 2005.

61. Bridgwater, A. V. and Peacocke, G. V. C. Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*, 4(1):1-73, 2000.

62. Sutton, D., Kelleher, B., and Ross, J. R. Review of literature on catalysts for biomass gasification. *Fuel Processing Technology*, 73(3):155-173, 2001.

63. Fukuda, H., Kondo, A., and Noda, H. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, 92(5):405-416, 2001.

64. Sun, Y. and Cheng, J. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83(1):1-11, 2002.

65. Galbe, M. and Zacchi, G. A review of the production of ethanol from softwood. *Applied Microbiology and Biotechnology*, 59(6):618-628, 2002.

66. Huber, G. W., Iborra, S., and Corma, A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews*, 106(9):4044-4098, 2006.

67. Huber, G.W., Chheda, J. N., Barrett, C. J., and Dumesic, J. A. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science*, 308(5727):1446-1450, 2005.

68. Marzialetti, T., Valenzuela Olarte, M. B., Sievers, C., Hoskins, T. J., Agrawal, P. K., and Jones, C. W. Dilute acid hydrolysis of Loblolly pine: A comprehensive approach. *Industrial & Engineering Chemistry Research*, 47(19):7131-7140, 2008.

69. Taherzadeh, M. J., Eklund, R., Gustafsson, L., Niklasson, C., and Lidén, G. Characterization and fermentation of dilute-acid hydrolyzates from wood. *Industrial & Engineering Chemistry Research*, 36(11):4659-4665, 1997.

70. Wyman, C. E., Dale, B. E., Elander, R. T., Holtzapple, M., Ladisch, M. R., and Lee, Y. Y. Coordinated development of leading biomass pretreatment technologies. *Bioresource Technology*, 96(18):1959-1966, 2005.

71. Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. Dissolution of cellose with ionic liquids. *Journal of the American Chemical Society*, 124(18):4974-4975, 2002.

72. Remsing, R. C., Swatloski, R. P., Rogers, R. D., and Moyna, G. Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a ^{13}C and $^{35/37}$Cl NMR relaxation study on model systems. *Chemical Communications*, (12):1271-1273, 2006.

73. Moulthrop, J. S., Swatloski, R. P., Moyna, G., and Rogers, R. D. High-resolution ^{13}C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions. *Chemical Communications*, (12):1557-1559, 2005.

74. Li, C. and Zhao, Z. K. Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid. *Advanced Synthesis & Catalysis*, 349(11-12):1847-1850, 2007.

75. Li, C., Wang, Q., and Zhao, Z. K. Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose. *Green Chemistry*, 10(2):177-182, 2008.

76. Sievers, C., Valenzuela-Olarte, M. B., Marzialetti, T., Musin, I., Agrawal, P. K., and Jones, C. W. Ionic-liquid-phase hydrolysis of pine wood. *Industrial & Engineering Chemistry Research*, 48(3):1277-1286, 2009.

77. Vanoye, L., Fanselow, M., Holbrey, J. D., Atkins, M. P., and Seddon, K. R. Kinetic model for the hydrolysis of lignocellulosic biomass in the ionic liquid, 1-ethyl-3-methyl-imidazolium chloride. *Green Chemistry*, 11(3):390-396, 2009.

78. Dong, K. and Zhang, S. Hydrogen bonds: a structural insight into ionic liquids. *Chemistry-A European Journal*, 18(10):2748-2761. 2012.

79. Bicker, M., Hirth, J., and Vogel, H. Dehydration of fructose to 5-hydroxymethylfurfural in sub-and supercritical acetone. *Green Chemistry*, 5(2):280-284, 2003.

80. Román-Leshkov, Y., Barrett, C. J., Liu, Z. Y. and Dumesic, J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature*, 447(7147):982-985, 2007.

81. Zhao, H., Holladay, J. E., Brown, H., and Zhang, Z. C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science*, 316(5831):1597-1600, 2007.

82. Yong, G., Zhang, Y., and Ying, J. Y. Efficient catalytic system for the selective production of 5-Hydroxymethylfurfural from glucose and fructose. *Angewandte Chemie*, 120(48):9485-9488, 2008.

83. Moreau, C., Finiels, A., and Vanoye, L. Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst. *Journal of Molecular Catalysis A: Chemical*, 253(1):165-169, 2006.

84. Bao, Q., Qiao, K., Tomida, D., and Yokoyama, C. Preparation of 5-hydroymethylfurfural by dehydration of fructose in the presence of acidic ionic liquid. *Catalysis Communications*, 9(6):1383-1388, 2008.

85. Hu, S., Zhang, Z., Zhou, Y., Han, B., Fan, H., Li, W., Song, J., and Xie, Y. Conversion of fructose to 5-hydroxymethylfurfural using ionic liquids prepared from renewable materials. *Green Chemistry*, 10(12):1280-1283, 2008.

86. Lansalot-Matras, C. and Moreau, C. Dehydration of fructose into 5-hydroxymethylfurfural in the presence of ionic liquids. *Catalysis Communications*, 4(10):517-520, 2003.

87. Sievers, C., Musin, I., Marzialetti, T., Valenzuela Olarte, M. B., Agrawal, P. K., and Jones, C. W. Acid-catalyzed conversion of sugars and furfurals in an ionic-liquid phase. *ChemSusChem*, 2(7):665-671, 2009.

88. Ray, D., Mittal, N., and Chung, W. J. Phosphorous pentoxide mediated synthesis of 5-HMF in ionic liquid at low temperature. *Carbohydrate Research*, 346(14):2145-2148, 2011.

89. Wei, Z., Li, Y., Thushara, D., Liu, Y., and Ren, Q. Novel dehydration of carbohydrates to 5-hydroxymethylfurfural catalyzed by Ir and Au chlorides in ionic liquids. *Journal of the Taiwan Institute of Chemical Engineers*, 42(2):363-370, 2011.

90. Jiang, F., Zhu, Q., Ma, D., Liu, X., and Han, X. Direct conversion and NMR observation of cellulose to glucose and 5-hydroxymethylfurfural (HMF) catalyzed by the acidic ionic liquids. *Journal of Molecular Catalysis A: Chemical*, 334(1):8-12, 2011.

91. Hu, L., Sun, Y., Lin, L., and Liu, S. Catalytic conversion of glucose into 5-hydroxymethylfurfural using double catalysts in ionic liquid. *Journal of the Taiwan Institute of Chemical Engineers*, 43(5):718-723, 2012.

92. Hu, L., Sun, Y., Lin, L., and Liu, S. 12-Tungstophosphoric acid/boric acid as synergetic catalysts for the conversion of glucose into 5-hydroxymethylfurfural in ionic liquid. *Biomass and Bioenergy*, 47:289-294, 2012.

93. Hu, L., Zhao, G., Tang, X., Wu, Z., Xu, J., Lin, L., and Liu, S. Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural over cellulose-derived carbonaceous catalyst in ionic liquid. *Bioresource Technology*, 148:501-507, 2013.

94. Zhou, X., Zhang, Z., Liu, B., Xu, Z., and Deng, K. Microwave-assisted rapid conversion of carbohydrates into 5-hydroxymethylfurfural by $ScCl_3$ in ionic liquids. *Carbohydrate Research*, 375:68-72, 2013.

95. Wang, S., Du, Y., Zhang, P., Cheng, X., and Qu, Y. One-pot synthesis of 5-hydroxymethylfurfural directly from cottonseed hull biomass using chromium

(III) chloride in ionic liquid. *Korean Journal of Chemical Engineering*, 31(12):2286-2290, 2014.

96. Xiong, Y., Zhang, Z., Wang, X., Liu, B., and Lin, J. Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst. *Chemical Engineering Journal*, 235:349-355, 2014.

97. Zhou, J., Xia, Z., Huang, T., Yan, P., Xu, W., Xu, Z., Wang, J., and Zhang, Z. C. An ionic liquid-organics-water ternary biphasic system enhances the 5-hydroxymethylfurfural yield in catalytic conversion of glucose at high concentrations. *Green Chemistry*, 17(8):4206-4216, 2015.

98. Zhang, H., Li, S., Song, X., Li, P., and Li, J. Preparation of 5-(hydroxymethyl) furfural by the catalytic degradation of cellulose in an ionic liquid/organic biphasic system. *BioResources*, 11(2):5190-5203, 2016.

99. Zhou, J., Tang, Z., Jiang, X., Jiang, R., Shao, J., Han, F., and Xu, Q. Catalytic conversion of glucose into 5-hydroxymethyl-furfural over chromium-exchanged bentonite in ionic liquid-dimethyl sulfoxide mixtures. *Waste and Biomass Valorization*, 7(6):1357-1368, 2016.

100. Nguyen, T. D., Nguyen, H. D., Nguyen, P. T., and Nguyen, H. D. Magnetic poly (vinylsulfonic-co-divinylbenzene) catalysts for direct conversion of cellulose into 5-hydroxymethylfurfural using ionic liquids. *Materials Transactions*, 56(9):1434-1440, 2015.

101. Shi, J., Yang, Y., Wang, N., Song, Z., Gao, H., Xia, Y., Li, W., and Wang, H. Catalytic conversion of fructose and sucrose to 5-hydroxymethylfurfural using simple ionic liquid/DMF binary reaction media. *Catalysis Communications*, 42:89-92, 2013.

102. Su, K., Liu, X., Ding, M., Yuan, Q., Li, Z., and Cheng, B. Effective conversion sucrose into 5-hydroxymethylfurfural by tyrosine in [Emim]Br. *Journal of Molecular Catalysis A: Chemical*, 379:350-354, 2013.

103. Xu, Q., Zhu, Z., Tian, Y., Deng, J., Shi, J., and Fu, Y. Sn-MCM-41 as efficient catalyst for the conversion of glucose into 5-hydroxymethylfurfural in ionic liquids. *Bio Resources*, 9(1):303-315, 2013.

104. Yi, Y. B., Ha, M. G., Lee, J. W., and Chung, C. H. New role of chromium fluoride: its catalytic action on the synthesis of hydroxymethylfurfural in ionic

liquid using raw plant biomass and characterization of biomass hydrolysis. *Chemical Engineering Journal*, 180:370-375, 2012.

105. Kuo, I. J., Suzuki, N., Yamauchi, Y., and Wu, K. C. W. Cellulose-to-HMF conversion using crystalline mesoporous titania and zirconia nanocatalysts in ionic liquid systems. *RSC Advances*, 3(6):2028-2034, 2013.

106. Zhang, Y., Pan, J., Gan, M., Ou, H., Yan, Y., Shi, W., and Yu, L. Acid-chromic chloride functionalized natural clay-particles for enhanced conversion of one-pot cellulose to 5-hydroxymethylfurfural in ionic liquids. *RSC Advances*, 4(23):11664-11672, 2014.

107. Tao, F., Song, H., and Chou, L. Dehydration of fructose into 5-hydroxymethylfurfural in acidic ionic liquids. *RSC Advances*, 1(4):672-676, 2011.

108. Tao, F. R., Zhuang, C., Cui, Y. Z., and Xu, J. Dehydration of glucose into 5-hydroxymethylfurfural in SO_3H-functionalized ionic liquids. *Chinese Chemical Letters*, 25(5):757-761, 2014.

109. Tong, X., Ma, Y., and Li, Y. An efficient catalytic dehydration of fructose and sucrose to 5-hydroxymethylfurfural with protic ionic liquids. *Carbohydrate Research*, 345(12):1698-1701, 2010.

110. Tong, X. and Li, Y. Efficient and selective dehydration of fructose to 5-hydroxymethylfurfural catalyzed by brønsted-acidic ionic liquids. *ChemSusChem*, 3(3):350-355, 2010.

111. Zhou, L., Liang, R., Ma, Z., Wu, T., and Wu, Y. Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids. *Bioresource Technology*, 129:450-455, 2013.

112. Ding, Z. D., Shi, J. C., Xiao, J. J., Gu, W. X., Zheng, C. G., and Wang, H. J. Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst. *Carbohydrate Polymers*, 90(2):792-798, 2012.

113. Shi, X. L., Zhang, M., Li, Y., and Zhang, W. Polypropylene fiber supported ionic liquids for the conversion of fructose to 5-hydroxymethylfurfural under mild conditions. *Green Chemistry*, 15(12):3438-3445, 2013.

114. Ma, Y., Qing, S., Wang, L., Islam, N., Guan, S., Gao, Z., Mamat, X., Li, H., Eli, W., and Wang, T. Production of 5-hydroxymethylfurfural from fructose by a

thermo-regulated and recyclable Brønsted acidic ionic liquid catalyst. *RSC Advances*, 5(59):47377-47383, 2015.

115. Ramli, N. A. S. and Amin, N. A. S. A new functionalized ionic liquid for efficient glucose conversion to 5-hydroxymethyl furfural and levulinic acid. *Journal of Molecular Catalysis A: Chemical*, 407:113-121, 2015.

116. Huang, P., Gu, A., and Wang, J. Efficient production of 5-hydroxymethylfurfural through the dehydration of sugars with caprolactam hydrogen sulfate ([CPL]HSO$_4$) ionic liquid catalyst in a water/proprylene glycol monomethyl ether mixed solvent. *Research on Chemical Intermediates*, 41(8):5311-5321, 2015.

117. Yang, Y., Liu, W., Wang, N., Wang, H., Li, W., and Song, Z. Effect of different ionic liquids on 5-hydroxymethylfurfural preparation from glucose in DMA over AlCl$_3$: experimental and theoretical study. *Chinese Journal of Chemistry*, 33(5):583-588, 2015.

118. Hu, S., Zhang, Z., Zhou, Y., Song, J., Fan, H., and Han, B. Direct conversion of insulin to 5-hydroxymethylfurfural in biorenewable ionic liquids. *Green Chemistry*, 11(6):873-877, 2009.

119. Hu, S., Zhang, Z., Song, J., Zhou, Y., and Han, B. Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl$_4$ in an ionic liquid. *Green Chemistry*, 11(11):1746-1749, 2009.

120. Jadhav, A. H., Kim, H., and Hwang, I. T. Efficient selective dehydration of fructose and sucrose into 5-hydroxymethylfurfural (HMF) using dicationic room temperature ionic liquids as a catalyst. *Catalysis Communications*, 21:96-103, 2012.

121. Qu, Y., Huang, C., Song, Y., Zhang, J., and Chen, B. Efficient dehydration of glucose to 5-hydroxymethylfurfural catalyzed by the ionic liquid, 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate. *Bioresource Technology*, 121:462-466, 2012.

122. Qu, Y. S., Song, Y. L., Huang, C. P., Zhang, J., and Chen, B. H. Alkaline ionic liquids as catalysts: a novel and green process for the dehydration of carbohydrates to give 5-hydroxymethylfurfural. *Industrial & Engineering Chemistry Research*, 51(40):13008-13013, 2012.

123. Walia, M., Sharma, U., Agnihotri, V. K., and Singh, B. Silica-supported boric acid assisted conversion of mono-and poly-saccharides to 5-hydroxymethylfurfural in ionic liquid. *RSC Advances*, 4(28):14414-14418, 2014.

124. Song, Y. L., Qu, Y. S., Huang, C. P., Ge, L. H., Li, Y. X., and Chen, B. H. Single-step conversion of cellobiose to 5-Hydroxymethylfurfural (5-HMF) catalyzed by poly ionic liquid. In *Advanced Materials Research*, 1004:885-890, 2014.

125. Qu, Y., Li, L., Wei, Q., Huang, C., Oleskowicz-Popiel, P., and Xu, J. One-pot conversion of disaccharide into 5-hydroxymethylfurfural catalyzed by imidazole ionic liquid. *Scientific Reports*, 6, 2016.

Chapter 5B

Investigation of PEG-6000 bridged -N-SO$_3$H functionalized geminal dicationic ionic liquids for catalytic conversion of fructose to 5-hydroxymethylfurfural

5B.1. Results and discussion

In this chapter, we have synthesized eight new members of two types of PEG-6000 bridged dicationic ionic liquids (DILs) with systematic structural variations of cations and anions of ionic liquids according to **Scheme 5B.1**. The cations varied were 2-methyl imidazole and diphenylamine and anions studied include trifluroacetate, trichloroacetate, acetate and hydrogen sulfate. Each ionic liquid was carefully characterized by FT-IR, ^{1}H and ^{13}C NMR, TGA and UV-Vis spectroscopy. The Brönsted acidities of these DILs were determined via the Hammett plot. The catalytic efficiencies of these ILs were explored as target specific acidic IL catalysts for the conversion of fructose to 5-hydroxymethylfurfural (HMF) in three different solvents, such as EtOAc, THF and CH$_3$CN using HPLC technique (**Scheme 5B.2**).

*Preliminary spectral analysis*
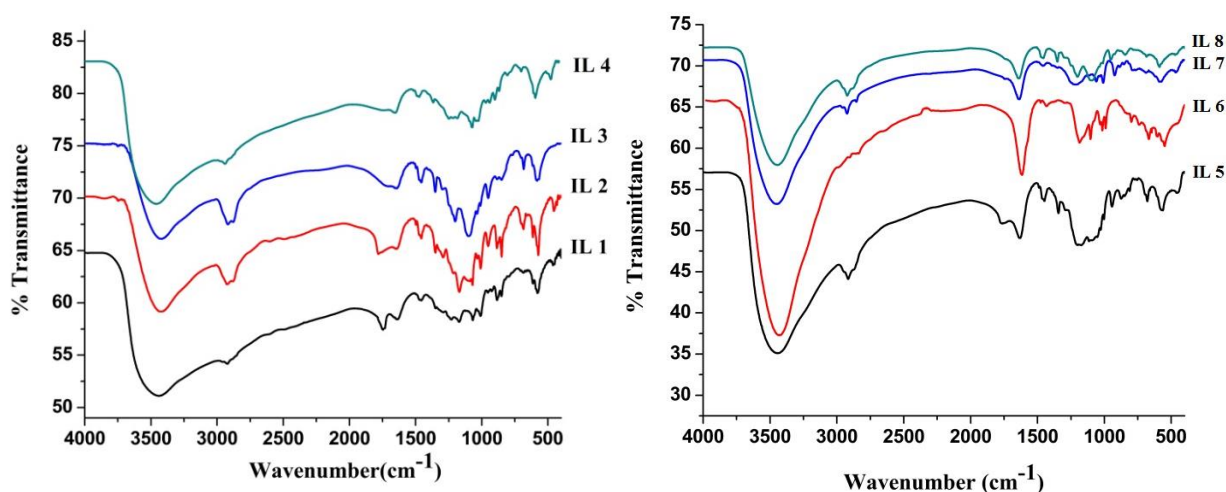
Fig. 5B.1a: FT-IR spectra of the PEG-6000 bridged DILs

FT-IR spectra of the two series of dicationic ILs are illustrated in **Fig. 5B.1a** and their assignments of various frequencies are listed in **Table 5B.1** and **Table 5B.2**. For all the ILs in the **Fig. 5B.1a,** we observe strong O-H stretching vibrations around 3416-3446 cm^{-1} for the –SO$_3$H group. The C-H stretching frequencies of methyl and methylene groups present in these ILs are appeared as strong, medium or weak intensities at 2925 cm^{-1}. The C-H bending vibration of both methyl and methylene groups shows peak at 1458-1469 cm^{-1}
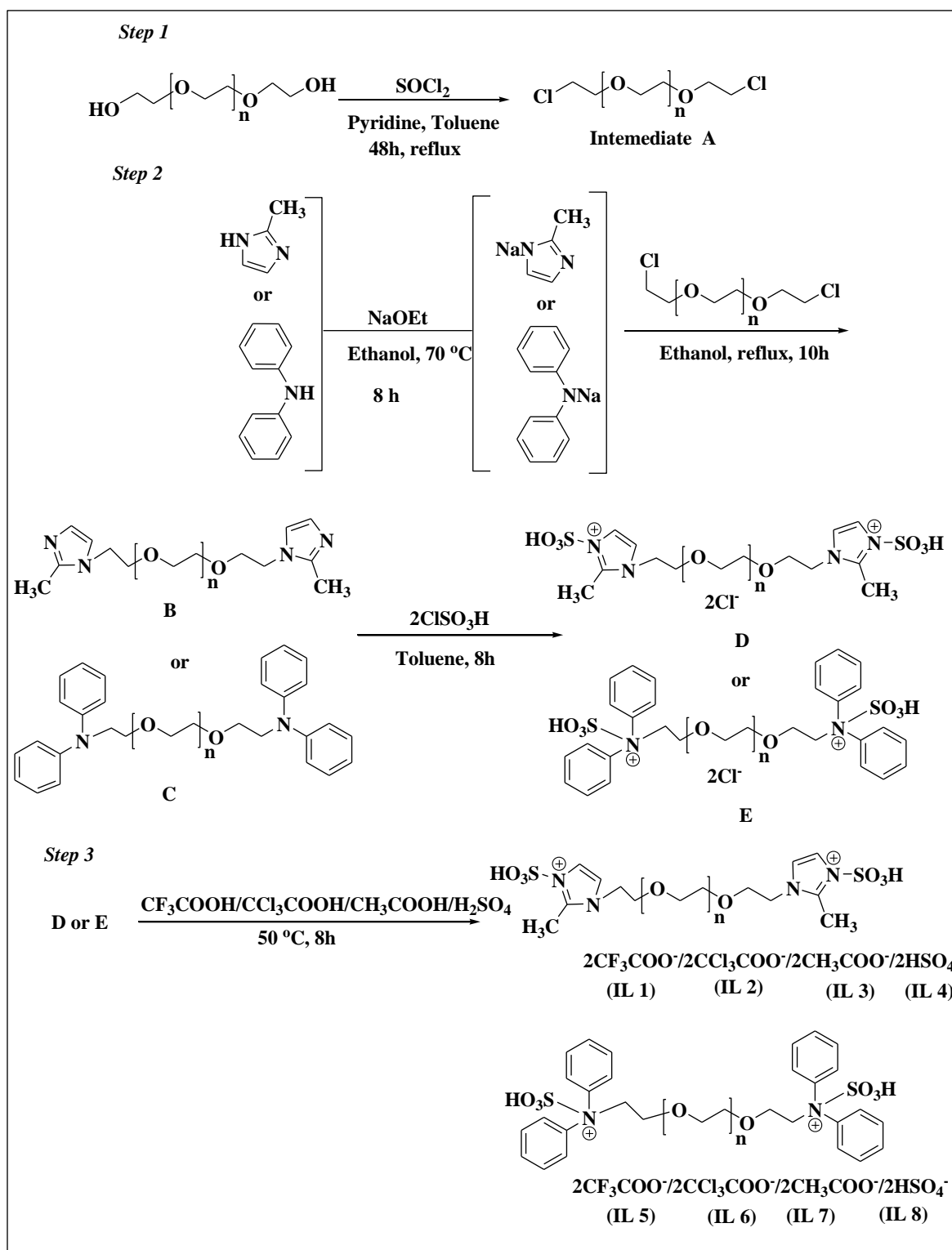
Scheme 5B.1: Preparation of PEG-6000 bridged dicationic ILs
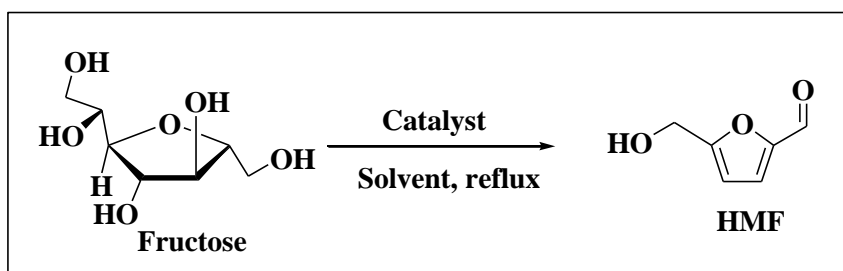
Scheme 5B.2: Conversion of fructose in to HMF in presence of PEG-6000 bridged DILs as catalyst

with variation of intensities. Another C-H bending vibration of –CH$_3$ group is observed around 1355-1367 cm^{-1} with different intensity peaks for the eight ILs. The carboxylate anions of imidazolium ionic liquids **IL 1** to **IL 3** display C=O stretching vibration at 1725-1786 cm^{-1} as strong to medium intensity band. This carbonyl peak is found around 1755-1776 cm^{-1} as medium strength peak for the diphenylammonium based ionic liquids **IL 5** to **IL 8**. All the four imidazolium ILs give C=C vibration as medium intensity at 1633-1644 cm^{-1} which are also overlapped by C=N stretching frequencies of imidazole ring.

The attachment of –SO$_3$H group in the imidazolium cation is confirmed via observation of S=O symmetric stretching at 1162-1233 cm^{-1} and asymmetric stretching around 1058-1100 cm^{-1} in addition to strong intensity bending vibration in the range of 577-588 cm^{-1} for the **IL 1** to **IL 4**. The position of C-C stretching and C-F asymmetric stretching of CF$_3$COO$^-$ group are also located in the same region of S=O symmetric stretching frequencies. The characteristic C-O/C-N stretch are also observed in the same range of S=O asymmetric vibrations for -O-CH$_2$-CH$_2$-O- bridging group attached with the N- atom of imidazolium/diphenyl ammonium cations. The typical C-O-C stretching for O-CH$_2$-CH$_2$-O bridging group is observed at 998-1018 cm^{-1} [1]. The eight ILs have unique N-S stretching vibrations around 843-897 cm^{-1} with weak to medium intensities. The aromatic C-H out of plane bending vibrations was observed at 678-698 cm^{-1}. The C-Cl stretching peak for CCl$_3$ group of trichloroacetate anion in **IL 2** and **IL 6** was observed at 855 cm^{-1} and 835 cm^{-1} respectively.

Table 5B.1: Observed FTIR bands and their assignment for ILs [DSMI-PEG$_{6000}$][CF$_3$COO$^-$]/[CCl$_3$COO$^-$]/[CH$_3$COO$^-$]/[HSO$_4^-$](vw = very weak; w = weak; m = medium, s = strong , b = broad; Str = stretch; bend = bending deformation; sym = symmetric; asym = asymmetric)

[DSMI-PEG$_{6000}$] [CF$_3$COO$^-$] IL1	[DSMI-PEG$_{6000}$] [CCl$_3$COO$^-$] IL2	[DSMI-PEG$_{6000}$] [CH$_3$COO$^-$] IL3	[DSMI-PEG$_{6000}$] [HSO$_4^-$] IL4	Assignments
3437(sb)	3416(sb)	3437(sb)	3427(sb)	O-H Str
2925(w)	2925(s)	2925(s)	2925(w)	C-H Str of CH$_3$- and -CH$_2$-
1746(m)	1786(m)	1725(m)	-	C=O Str
1644(m)	1644(m)	1644(m)	1633(m)	C=C/C=N Str
1469(m)	1469(s)	1458(s)	1469(m)	C-H bend of CH$_3$- and –CH$_2$- group
1367(vw)	1367(vw)	1356(s)	1356(vw)	C-H bend of CH$_3$- group
1182(m)	-	-	-	C-F Str
1233(w)	1166(s)	1202(s)	1162(w)	S=O sym /C-C Str
1058(m)	1063(m)	1100(s)	1058(m)	S=O asym/C-O/C-N Str
998(m)	1007(vw)	1010(m)	998(vw)	C-O-C Str
895(m)	897(m)	886(w)	886(w)	N-S Str
--	855(s)	----	---	C-Cl Str
691(vw)	691(s)	691(s)	691(w)	Out of plane C=C-H bend
577(s)	575(s)	577(s)	588(s)	S=O bend

Table 5B.2: Observed FTIR bands and their assignment for ILs [DSDPA-PEG$_{6000}$][CF$_3$COO$^-$]/[CCl$_3$COO$^-$]/[CH$_3$COO$^-$]/[HSO$_4^-$](vw = very weak; w = weak; m = medium, s = strong; b = broad; Str = stretch; bend = bending deformation; sym = symmetric; asym = asymmetric)

[DSDPA-PEG$_{6000}$] [CF$_3$COO$^-$] IL 5	[DSDPA-PEG$_{6000}$] [CH$_3$COO$^-$] IL 6	[DSDPA-PEG$_{6000}$][HSO$_4^-$] IL 7	[DSDPA-PEG$_{6000}$] [CCl$_3$COO$^-$] IL 8	Assignments
3446(sb)	3443(s)	3446(s)	3446(s)	O-H Str
2925(m)	-	2924(m)	2913(m)	C-H Str of CH$_3$- and -CH$_2$- Str
1776(m)	1765(m)	1755 (m)	-	-C=O Str
1644(s)	1643(s)	1632(s)	1632(s)	-C=C- bend

1458(m)	1450(vw)	1462(vw)	1468(m)	C-H bend of CH_3- and $-CH_2$- group
1190(w)	-	-	-	-C-F Str
1193(m)	1211(s)	1222(s)	1192(m)	S-O sym /C-C Str
1110(s)	1131(m)	1057(m)	1089(s)	S=O asym/C-O / C-N Str
886(vw)	884(w)	885(vw)	843(m)	N-S Str
679(m)	698(w)	678(vw)	689(w)	Out of plane C=C-H bend
588(s)	573(m)	576(m)	587(s)	S=O bend
-	835(w)	-	-	C-Cl Str

The ^1H and ^{13}C NMR spectra of imidazolium based DIL with acetate anion (**IL 3**) and diphenyl ammonium based DIL with HSO_4^- anion (**IL 8**) are represented in **Fig. 5B.1b** and **Fig. 5B.1c**. The presence of acetate anion in **IL 3** was evidenced from the -CH_3 peak of -OAc at 1.85 ppm in ^1H NMR spectrum and also from the C=O peak at 172.6 ppm in the ^{13}C NMR spectrum of the IL **(Fig. 5B.1b)**. The repeating unit of PEG chain -OCH_2-CH_2O- displays one broad singlet at 6.67 ppm for the two methylene group protons in the ^1H NMR spectrum and a peak at 70.2 ppm in ^{13}C NMR spectrum. The chemical shift position of two doublets for four protons at 7.46 and 7.11 ppm in aromatic region support the attachment of two imidazole ring on the geminal positions of PEG bridging group in the DIL. The ^1H and ^{13}C NMR spectra for diphenylammonium based IL with HSO_4^- anion (**IL 8**) also gives similar peak for the protons of PEG-linker at 5.05-5.14 ppm and at 72.3 ppm for the carbons of repeating unit respectively as displayed in **Fig. 5B.1c**.
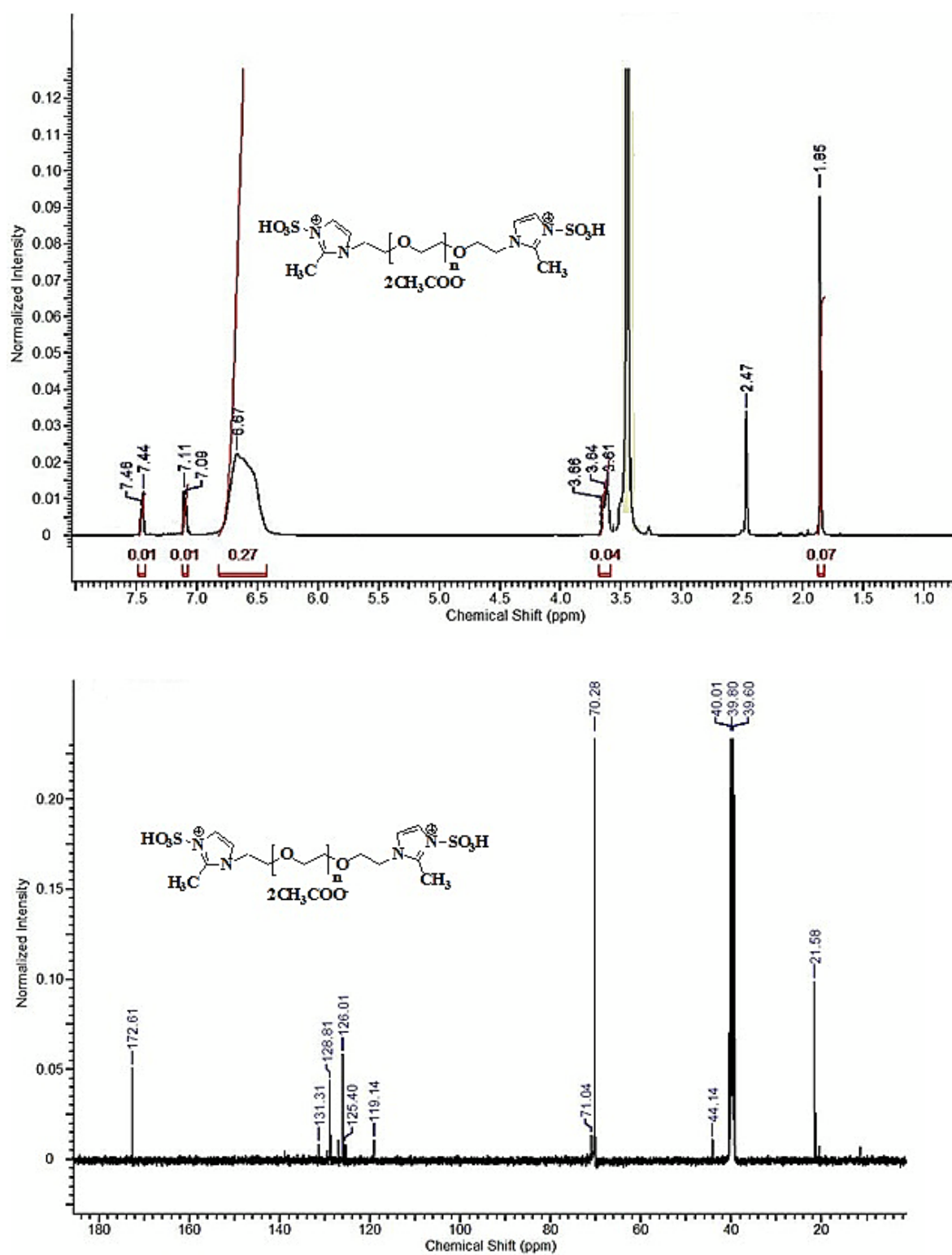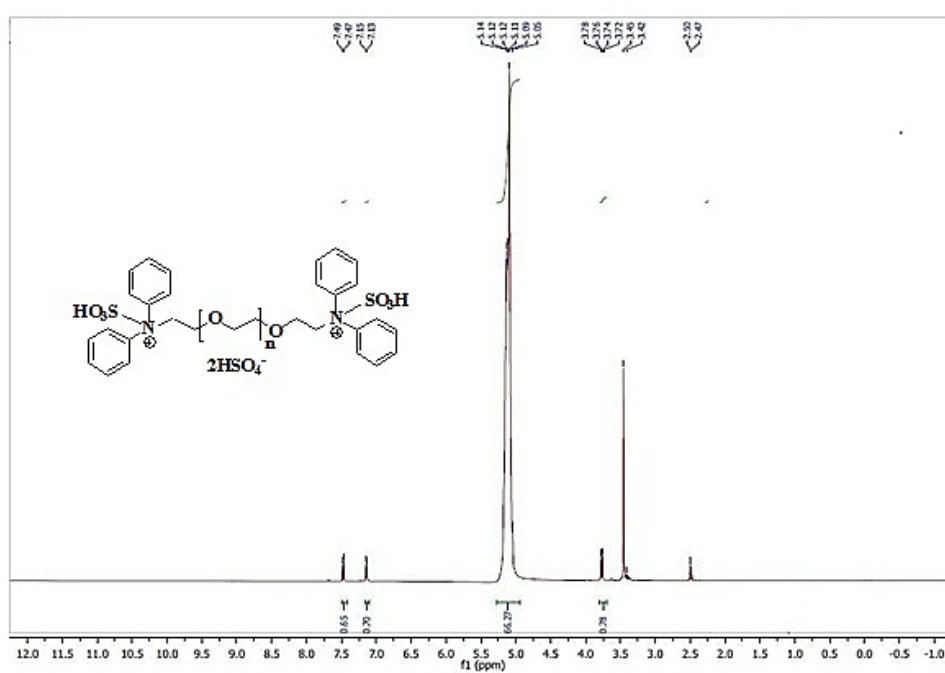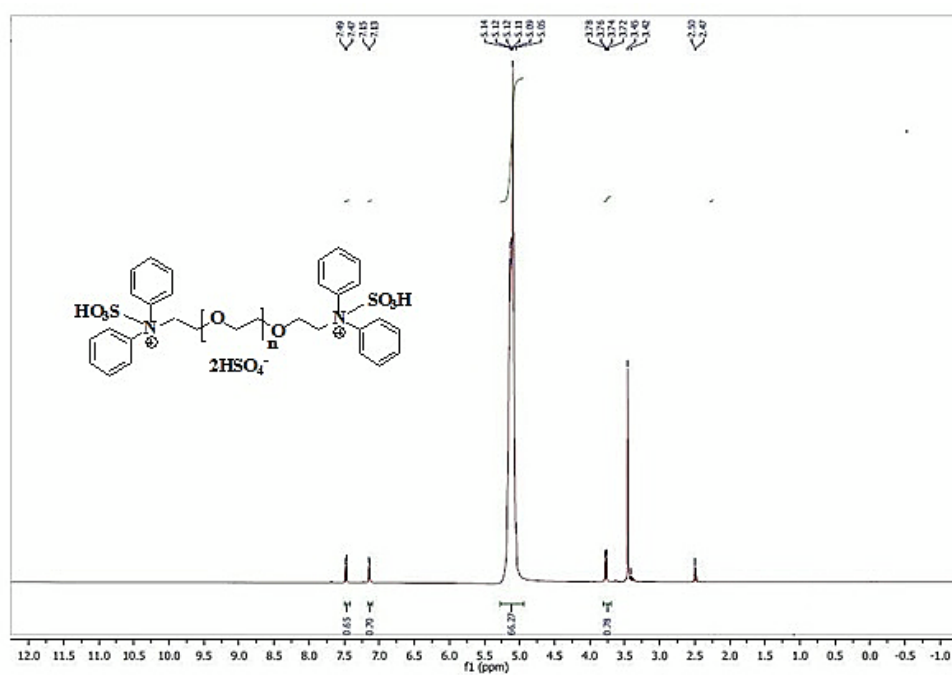
Fig. 5B.1b: ¹H NMR and ¹³C NMR spectrum of **IL 3**

Fig. 5B.1c. ^{1}H NMR and ^{13}C NMR spectra of **IL 8**

TGA analysis

The thermo gravimetric analyses of the DILs are presented in **Fig. 5B.2**. Among the imidazolium based four ILs, **IL 1** with trifluoroacetate anion was found to be more thermally stable than the ionic liquids possessing other anions such as CCl_3COO^-, AcO^- and HSO_4^-. All the four 2-methyl imidazolium cation containing ILs seemed to be stable up to 150 °C. Out of the four anions varied, it is the CF_3COO^- anion which seemed to interact best with its cation, while HSO_4^- containing IL was the most loosely held. In case of diphenylamine based four ILs, **IL 6** with CCl_3COO^- anion was more stable up to 200 °C than the three other ILs. The TGA patterns of both series of DILs express no weight loss of physisorbed water near 100 °C.
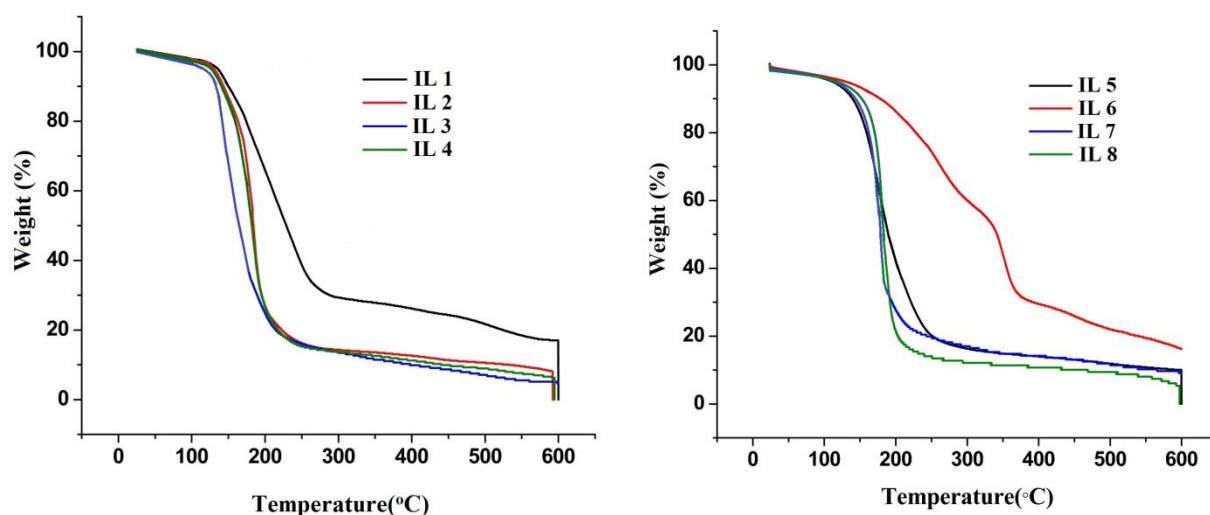
Fig. 5B.2: TGA profile of the DILs

Miscibility properties of the DILs with solvents

The solubility properties of all dicationic ILs were investigated in water, polar and non-polar organic solvent at room temperature and the results are illustrated in **Table 5B.3**. It can be seen from the table that, owing to the capability of $–SO_3H$ groups of the ILs as well as the carboxylate anions to form hydrogen bonds or other secondary interactions with varying strengths, they tend to be more soluble in polar-protic and aprotic organic solvents.

Table 5B.3: Solubility study of DILs at room temperature

Ionic Liquids	EtOH	H$_2$O	CH$_3$CN	Acetone	THF	EtOAc	Hexane	Et$_2$O	Toluene	DCM
IL 1	s	s	s	s	s	i	i	i	i	i
IL 2	s	s	s	s	s	i	i	i	i	i
IL 3	s	s	s	s	s	i	i	i	i	i
IL 4	s	s	s	s	s	i	i	i	i	i
IL 5	s	s	s	s	s	i	i	i	i	i
IL 6	s	s	s	s	s	i	i	i	i	i
IL 7	s	s	s	s	s	i	i	i	i	i
IL 8	s	s	s	s	s	i	i	i	i	i

s: soluble; i: insoluble

Hammett acidity determination of the ILs

The acid strength of the -SO$_3$H functionalized PEG-6000 bridged dicationic ILs were estimated via Hammett indicator method by following the same procedure as included in the previous **Chapter 1C** using 4-nitroaniline as the basic indicator. The procedure required equal mixing of the indicator (5 M) and catalysts (equal amount of all) solution in ethanol. The absorbance of the basic indicator decreases with increasing acidic strength of the ILs. The maximum absorbance for the indicator was observed at 378 nm in ethanol (**Fig. 5B.3**).
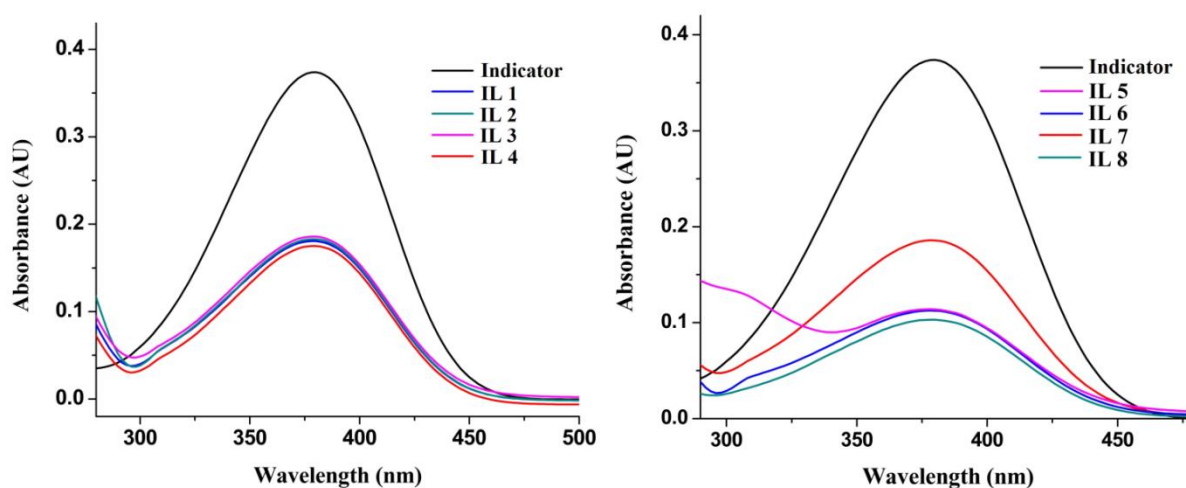

Fig. 5B.3: Hammett plot of the DILs

Table 5B.4: Determination of Hammett acidity of the –SO$_3$H functionalized dicationic ionic liquids

Sample name	A$_{max}$	[I]%	[IH]%	H^o
Blank	0.376	100	0	-
IL 1	0.183	48.67	51.33	0.967
IL 2	0.187	49.73	50.27	0.985
IL 3	0.184	48.93	51.07	1.340
IL 4	0.176	46.80	53.2	0.934
IL 5	0.113	30.05	69.95	0.623
IL 6	0.115	30.59	69.41	0.634
IL 7	0.260	69.15	30.85	0.971
IL 8	0.104	27.66	72.34	0.572

The highest acidity was observed for the two ILs of bisulfate anion such as **IL 4** of imidazoliumcation and **IL 8** of diphenylammoniumcation followed by the ILs of trifluoroacetate anion (**IL 1** and **IL 5**). The acetate anion bearing two ILs (**IL 3** and **IL 7**) showed lowest acidic nature among the four anions for the two series of dicationic ILs. The acidity order found for the eight ILs in increasing order is (**Table 5B.4**): **IL 3<IL 7<IL 2<IL 1<IL 4<IL 6<IL 5<IL 8**.

Evaluation of catalytic dehydration of fructose into 5-hydroxy methyl furfural (HMF)

The catalytic efficiencies of the **IL 1-8** were evaluated for the fructose dehydration reaction under reflux temperature in different organic solvents. The quantitative analyses of HMF formation were monitored by HPLC method in presence of C-18 reverse phase column and UV-detector for identification of maximum λ_{HMF} at 284 nm. The detail procedure of analytical method is included in **Experimental section** of this Chapter. The concentration of HMF in each sample of reaction mixture was calculated from a standard curve of HMF solutions of known concentrations (10, 20, 30, 40, and 50 ppm) in **Fig. 5B.4**.
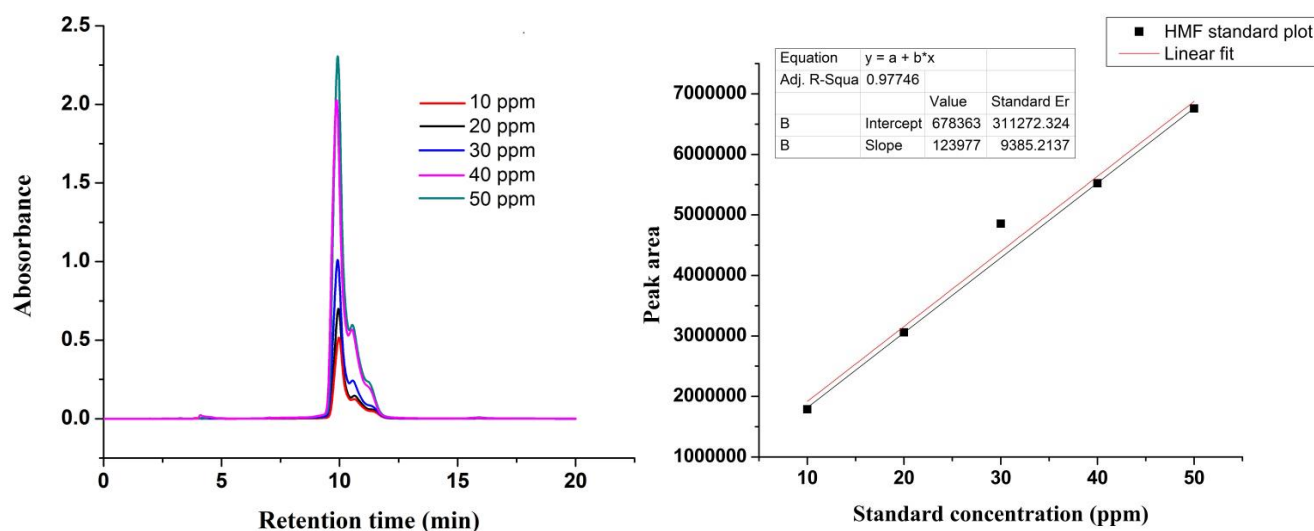
Fig. 5B.4: Calibration graph for standard HMF concentrations

## *Influence of IL 8 dosage on fructose dehydration*

In this study, different dosage of most acidic diphenylamine based **IL 8** was initially screened for optimization of catalyst amount in acetonitrile under reflux temperature for selective dehydration of fructose to HMF during 3.5 h reaction time expressed in **Table 5B.5**.

Table 5B.5: Optimization of catalyst amount **IL 8** at 75 °C in CH$_3$CN

Entry	IL 8 Amount (mol%)[a, b]	Time(h)	% Conversion of fructose	% Yield of HMF
1	5	3.5	91.2	61.2
2	10	3.5	94.5	65.4
3	15	3.5	100	73
4	20	3.5	95.4	63.2
5	25	3.5	89.2	60.7

[a]Weight mol% of catalyst with reference to molecular weight of fructose; [b]Calculated from the HPLC analysis

Fig. 5B.5 shows the influence of **IL 8** dosages on selective dehydration of fructose to HMF in CH$_3$CN.The amounts of IL used were 5, 10, 15, 20 and 25 mol% of weight with reference to molecular weight of fructose.
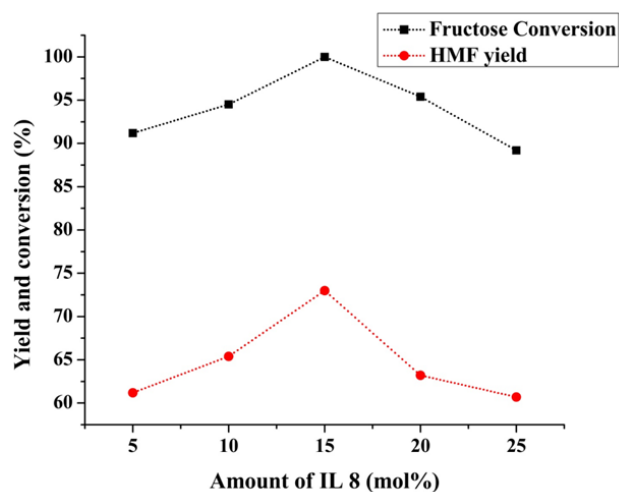
Fig. 5B.5: Influence of **IL 8** amount on fructose conversion and HMF yield

From the figure**,** it is evident that when only 5 mol% of **IL 8** was employed, 91.2 % fructose conversion was achieved with 61.2% HMF yield. The gradual increasing of **IL 8** amounts up to 15 mol%, achieved 100% conversion of the fructose with 73% HMF yield. However, on further increase of catalyst dosage to 20 mol%, both the fructose conversion and HMF yield decreased. It might be due to prevailing side reactions such as rehydration of HMF, aldol condensation etc. with increasing catalyst amount. Therefore, the best selective formation of HMF was achieved at 73% yield for 100% conversion fructose with 15 mol% of **IL 8.**

Effect of different solvents on fructose conversion

The above optimized amount of **IL 8** was extended for evaluation of the catalytic activities of all the eight DILs for the dehydration of fructose to HMF in three different polar aprotic solvents such as EtOAc, THF and CH$_3$CN under reflux conditions **(Fig. 5B.6 & 7).** In this study, we avoided the use of polar protic solvent for possible greater extent of intermolecular H-bonding abilities with the catalyst, substrate and final product HMF, and then associated problems for separation of the HMF during work-up steps. The results of solvent studies results are summarized in **Table 5B.6** and **Table 5B.7** separately for diphenylammonium/imidazolium based DILs. The acidities of the ILs showed significant influence on the fructose conversion to HMF. The nature of the anion also influences the catalytic activity of these ILs. The progress of the reactions was monitored via HPLC analysis. The HPLC profile of each catalytic systems displayed single peak formation of HMF during analysis.

Table 5B.6: Effect of different solvent on the catalytic activity of **IL 1-4** under reflux temperature

Solvent	Time(h)	% Conversion[a]			
		IL 1	**IL 2**	**IL 3**	**IL 4**
EtOAc	3	4.6	76.5	45.6	17.9
	4	5.9	84.3	51.2	20.4
	6	-	100	-	-
	12	35.6	-	100	34.9
THF	3	10.1	3.9	3.5	22.2
	4	23.2	7.3	3.9	34.7
	12	64.2	58.4	56.2	67.6
CH$_3$CN	3	46.2	15.1	16.8	30.5
	4	56.3	20.5	27.2	47.7
	12	100	63.7	33	100

[a] Calculated from the HPLC analysis
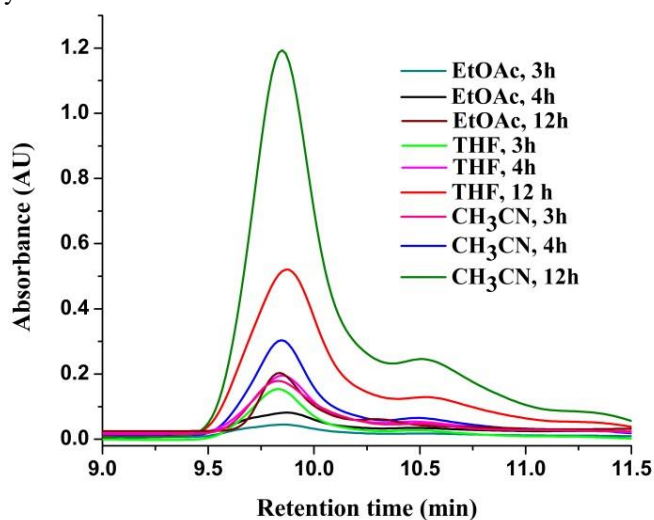
Fig. 5B.6: Fructose conversion in different solvents with 15 mol% of **IL 4** as catalyst

Table 5B.7: Effect of different solvent on the catalytic activity of **IL 5-8** under reflux temperature

Solvent	Time (h)	% Conversion[a]			
		IL 5	**IL 6**	**IL 7**	**IL 8**
EtOAc	3	6.2	86.4	78.9	65.3
	4	12.2	100	-	85.8

	5	-	-	100	100
	12	56.2	-	-	-
THF	3	47.2	43.2	2.5	47.6
	4	56.7	49.8	14.7	47.6
	12	80.4	78.2	61.3	2.7
CH$_3$CN	3	87.3	25.4	75.6	100
	4	100	36	96.5	-
	12	-	100	-	-

[a]Calculated from the HPLC analysis
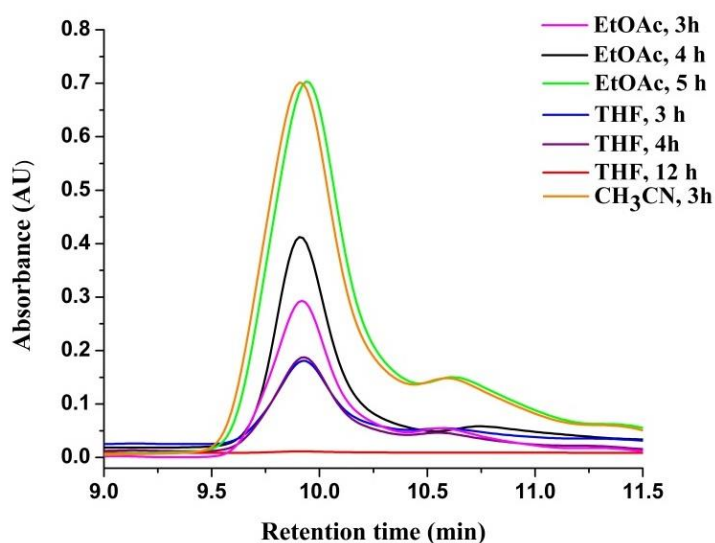
Fig. 5B.7: Fructose conversion in different solvents with 15 mol% of **IL 8** as catalyst

From the screening, CH$_3$CN and EtOAC seem to be the best solvent for both the type of DILs, while **IL 3** in THF proves to be as mild reaction medium.

In case of 2-methyl imdazolium based ILs with varied anions, 100% conversion of fructose in ethyl acetate was observed within 6 h reaction for **IL 2** and 12 h reaction for **IL 3** (**Table 5B.6**). It can be expected due to weak ion-pair interaction of acetate anion with the cation of **IL 3**. Using acetonitrile as reaction medium, the **IL 1** and **IL 4** showed 100% conversion of fructose during 12 h reaction in spite of their different Brönsted acidities as found in the Hammett plot.

For diphenylammonium based ILs with varied anions, we observed best catalytic activity for **IL 8** in ethyl acetate and acetonitrile within 3-5 h reaction under reflux conditions (**Table 5B.7**). Two other diphenylammonium ionic liquids **IL 6** and **IL 7** also displayed good catalytic conversion for the dehydration of fructose to HMF during

4-5 h reaction in ethyl acetate. **IL 5** also showed 100% conversion of fructose to HMF for 4 h reaction in acetonitrile. We observed almost comparable catalytic activities of the **IL 5** and **IL 8** in acetonitrile containing HSO_4^- and CF_3COO^- anions respectively.

Out of the two series of DILs, the most acidic **IL 8** displayed the best catalytic activity in CH_3CN at its reflux temperature. The percentage conversion of fructose obtained using different acidic strength ILs in these three solvents are not in accordance with the acidity order obtained from the Hammett plot. They are found slightly different depending on the nature of solvents. However, in some cases 100% fructose conversion was achieved according to the same acidity order of the Hammett plot as presented in both the tables. At present, we didn't find any concrete reason for this variation. The ion-pair strength of IL and its interaction with the substrate fructose molecule in a particular solvent may be the key factor for catalytic activity of these ILs.

Effect of anions on the extraction of HMF from the reaction mixture

To know the effect of anions on percentage yield of HMF, **IL 5-8** were employed as catalysts. It is evident from the **Fig. 5B.8** that nature of anions indeed plays a part in the efficient extraction of HMF from the reaction mixture. The results suggest that anions with stronger hydrogen bond accepting ability have stronger interaction with HMF and hence the separation of HMF became increasingly difficult. From this study, the formation abilities of hydrogen bonds of the anions with the –OH group of HMF were found to decrease in the order: $CH_3COO^- > HSO_4^- > CCl_3COO^- > CF_3COO^-$
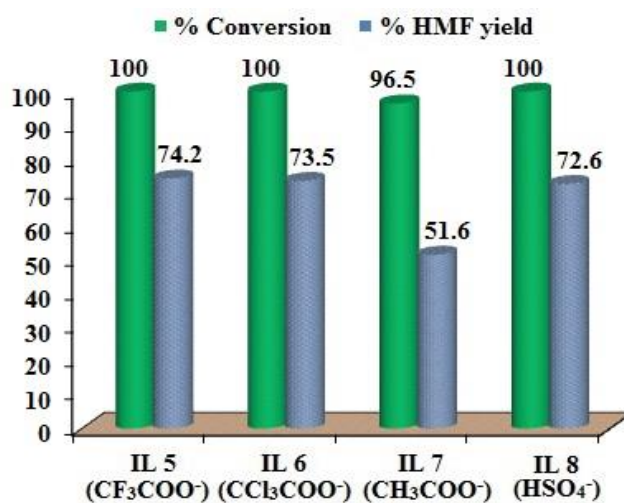

Fig. 5B.8: Effect of the nature of anions on extraction of HMF

Recycling of catalyst IL 5

To study the reusability of **IL 5**, HMF was extracted from the reaction mixture using water-EtOAc as the extraction phase. **Fig. 5B.9** illustrates the reusability study of **IL 5.** After the first cycle of reaction in EtOAc was over, 10mL of distilled water was added. Subsequently, HMF was separated from the reaction mixture by continuous extraction with small aliquots of EtOAc. The amount of extracted product was determined by HPLC. It demonstrated that 65-73% product extraction was possible with EtOAc. After extraction, the catalyst was dried in vacuum oven to remove the water and residual EtOAc. The dried IL could be reused for three more cycles with good reproducibility.

The decreasing catalytic activity of the IL with increasing cycle numbers may be attributed to the blocking of the catalytic sites by the residual HMF in the previous cycle. This inefficient extraction of the resulting product in the previous run strongly influences the results of the recycling test. Hence, efficient extraction of HMF from the reaction mixture will remain the topic of future studies.
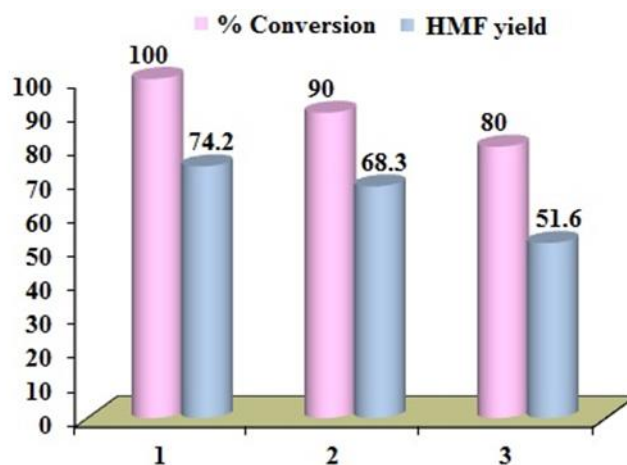
Fig. 5B.9: Reusability profile of **IL 5**

5B.2. Conclusion

In conclusion, we have synthesized two series of PEG-6000 based dicationic diphenylammonium/imidazolium based ILs through variation of four anions CF_3COO^-, CCl_3COO^-, AcO^- and HSO_4^- as target oriented acidic IL catalysts for the dehydration of fructose in to HMF in polar aprotic solvent. The DILs were characterized with various analytical techniques including NMR, FT-IR, TGA and Hammett acidity studies. The

acid strength of the ILs seemed to play a significant role in the outcome of the reaction. Though the ILs were strongly acidic in nature, it did not affect the selectivity of HMF in the reaction. Single peak pertaining to presence of only HMF was evident from the HPLC analysis. The dosage of the catalyst also had an impact on the outcome of the reaction. The efficient extraction of HMF was strongly influenced by the nature of the anion used in the ILs. The anions with stronger hydrogen bonding formation ability had a negative impact on the extraction process. This factor also affected the recyclability test by blocking the active catalytic sites for further reaction.

5B.3. Experimental section

General Remarks

The chemicals used in this study were purchased from different reputed chemical suppliers in pure state. The synthesized PEG-6000 bridged DILs were characterized via FT-IR, ^{1}H NMR and ^{13}C NMR, TGA, UV-Vis spectrophotometer.

General procedure for synthesis of PEG$_{6000}$-DILs

The synthetic process of PEG-6000 bridged geminal DILs involved in three steps according to reaction **Scheme 5B.1.**

Step I: Synthesis of oligo(ethylene glycol)dichloride(Intermediate *A*):

In a three necked 100 ml round bottomed flask equipped with a condenser, magnetic stirrer and N_2 inlet, a mixture of 12 gm (2 mmol) of PEG (M_n=6000 g/mol) and 0.871 mL (12 mmol) of $SOCl_2$ in 50 mL of freshly dried toluene was refluxed for 48 h fitted with calcium guard tube in presence of 0.967 mL (12 mmol) of pyridine with continuous stirring in a fume hood. The solvent was evaporated under reduced pressure and the resulting solid washed with diethyl ether to yield intermediate **A** in analytically pure state.

Step II: Synthesis of -SO$_3$H functionalized PEG$_{6000}$-DIL (Intermediate **D/E**):

At first an equimolar mixture of 2-methylimidazole/diphenyl amine (1 mmol) and sodium ethoxide (1mmol) was stirred in ethanol (95%) (30mL) at room temperature for 8 h. After that solvent was removed under reduced pressure, washed the residue with diethyl ether three times and dried in vacuum to give the sodium salt of 2-

methylimidazole/diphenylamine. Subsequently, the salt was treated with 2.962 gm (0.5 mmol) of oligo(ethylene glycol)dichloride by dissolving it in ethanol (50 mL) and the mixture was refluxed for 10 h and filtered. The filtrate was washed with ether for three times, and then evaporated under reduced pressure to give the respective intermediate **B/C** as brown solid. In the next step, $ClSO_3H$ (3 mmol) was added dropwise in to the solution of intermediate **B/C** in dry toluene (20 mL) in 30 min and the mixture was stirred for 8h. The solvent was evaporated under reduced pressure and the remaining part was washed three times (3×5 mL) with dry toluene to yield the intermediate **D/E.**

Step III*: Metathesis reaction of intermediate **D/E***:

In the final step, $CF_3COOH/CCl_3COOH/CH_3COOH/H_2SO_4$ (3 mmol) was added dropwise in dry toluene within 30 min at ambient temperature. The final solution was stirred at 50 °C for another 8h and evaporated under reduced pressure to give PEG_{6000}-DIL as a viscous light yellow/brown liquid.

General procedure for synthesis of 5-hydroxy methyl furfural

In a typical reaction procedure, fructose (1 mmol), PEG_{6000}-DIL (15 mol% with reference to molecular weight of fructose) and solvent (5 mL) were added in to a 50 mL round bottomed flask. The reaction mixture was stirred vigorously and refluxed in an oil bath for specific time (**Table 5B.5** and **5B.6**). Reaction aliquots (0.1 mL) were collected after definite time interval and they were diluted to 2 mL using ultrapure water as the diluent. The reaction mixtures were analyzed by HPLC to determine the percentage yield of HMF.

Analytical Methods

Quantitative analyses of HMF were performed by HPLC using a C_{18}-reverse phased column (200 mm $\times$ 4.6 mm) equipped with an UV detector (λ_{HMF} = 284 nm) (Waters 2489). For the detection of HMF, a 10:90 (v/v) mixture of acetonitrile and water was used as the mobile phase at a flow rate of 0.6 mL/min. The column temperature was maintained at 25 °C. The volume of each injection was 20 μL. HMF in the samples was identified by retention time determined using pure samples. The concentration of HMF in the samples was determined from a standard curve obtained with samples of HMF of known concentrations (10, 20, 30, 40 and 50 ppm).
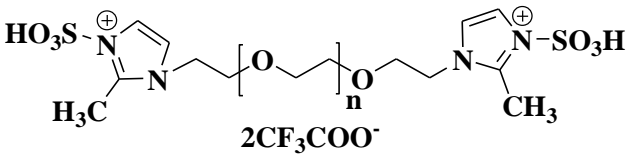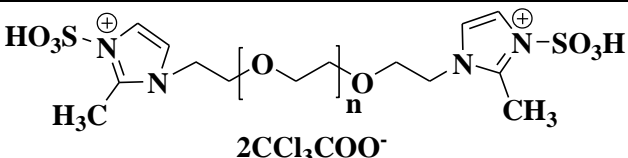
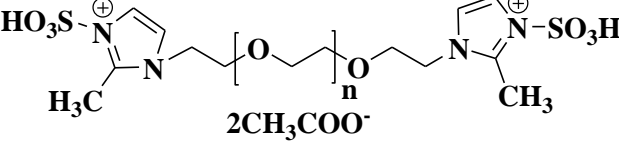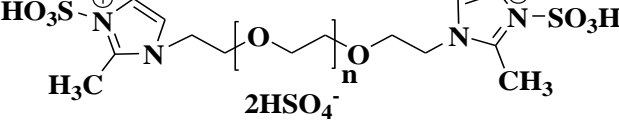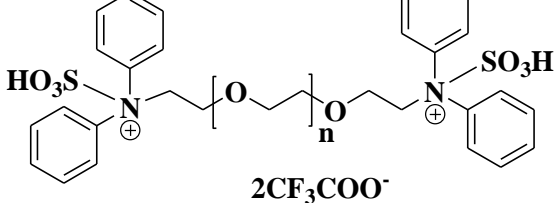The yield of HMF was calculated as follows:

Mass of HMF (mg) = [HMF concentration on sample (mg/mL)] × [Volume of the reaction mixture (V_{RM})] × [dilution factor (DF)]
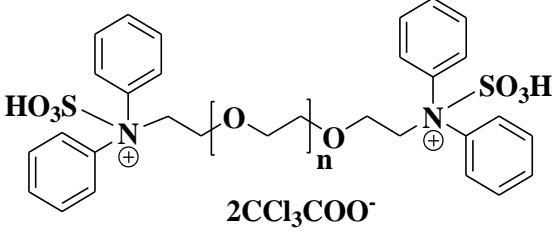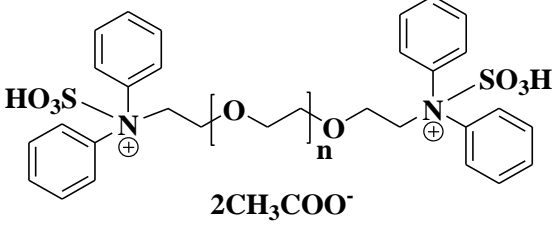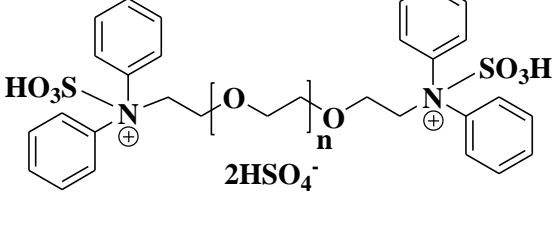
Where V_{RM} = 0.1mL, DF = 20

HMF yield (wt %) = [mass of HMF (mg)/ mass of fructose (mg)]×100

5B.4. Spectral data of DILs

Product	Spectral data
  IL 1	Brown viscous liquid; FT-IR(KBr): 3437, 2925, 2597, 1746, 1633, 1469, 1367, 1233, 1182, 1058, 998, 895, 844, 577 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.2 (broad singlet, -OCH$_2$-OCH$_2$-O unit), 7.48 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 3.64-3.61 (m, 8H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, DMS0-d$_6$): δ 159.2, 158.9, 139.5, 131.6, 129.1, 127.1, 126.1, 125.6, 117.1, 114.2, 70.4, 21.3.
  IL 2	Brown viscous liquid; FT-IR(KBr): 3416, 2925, 2862, 2586, 2474, 1786, 1644, 1469, 1362, 1300, 1166, 1063, 1010, 948, 897, 855, 691, 628,575 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.52-7.50 (d, J = 8.0 Hz, 2H), 7.23-7.21 (broad singlet, -OCH$_2$-OCH$_2$-O unit) , 7.15-7.11 (m, 2H), 3.65-3.62 (m, 8H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 159.1, 132.1, 129.5, 125.9, 125.4, 69.6, 55.4, 43.1, 20.5.

  IL 3	Brown viscous liquid; FT-IR(KBr): 3427, 2925, 2874, 1725, 1644, 1458, 1356, 1202, 1100, 1018, 1007, 946, 886, 833, 691, 577 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.46 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.67 (broad singlet, -OCH$_2$-CH$_2$-O- unit), 3.66-3.61 (m, 8H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 172.4, 131.0, 128.8, 126.0, 125.4, 119.1, 70.3, 44.1, 21.6.
  IL 4	Brown liquid; FT-IR(KBr): 3437, 2925, 1746, 1633, 1469, 1356, 1233, 1162, 1058, 998, 946, 916, 886, 844, 782, 691, 588 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.50-7.48 (d, J = 8.0 Hz, 2H), 7.15-7.13 (d, J= 8.0 Hz, 2H), 4.81 (broad singlet, -OCH$_2$-OCH$_2$-O unit), 3.43-3.39 (m, 8H), 1.11-1.08 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 128.5, 125.7, 70.0, 61.7, 21.0.
  IL 5	Brown viscous liquid; FT-IR(KBr): 3446, 2925, 1776, 1644, 1458, 1356, 1193, 1110, 1007, 946, 886, 579, 588 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.51-7.49 (m, 8 H), 7.15-7.13 (m, 12H), 5.59-5.47 (broad singlet, -OCH$_2$-OCH$_2$-O unit), 3.67-3.63 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ159.0, 158.7, 128.7, 126.0, 122.1, 118.9, 114.1, 70.2, 60.7.

IL 6	Brown viscous liquid; FT-IR(KBr): 3443, 2850, 1643, 1462, 1211, 1131, 1028, 835,767, 698, 573 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.74 (broad singlet, -OCH$_2$-OCH$_2$-O unit), 7.18-7.16 (m, 8H), 7.11-7.09 (m, 12 H), 3.64-3.61 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.6, 137.8, 131.3, 129.4, 126.7, 126.0, 120.2, 117.2, 70.3, 66.7.
IL 7	Brown viscous liquid; FT-IR (KBr): 3446, 2924, 2852, 1755, 1632, 1468, 1222, 1057, 1006, 924, 792, 678, 578 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.42-2.49 (m, 10 H), 7.14-7.13 (m, 10H), 5.05-5.14 (broad singlet, -OCH$_2$-CH$_2$O- unit), 3.72-3.78 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.5, 142.1, 139.3, 133.8, 131.2, 126.1, 72.3, 64.9, 59.9.
IL 8	Brown liquid; FT-IR (KBr): 3446, 2913, 1745, 1632, 1468, 1355, 1192, 1089, 955, 843, 689, 587 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (broad singlet, -OCH$_2$-OCH$_2$-O unit), 7.18-7.16 (m, 8H), 7.11-7.10 (m, 12 H), 3.67-3.61 (m, 8H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6: δ 163.3, 137.8, 128.7, 126.0, 125.8, 124.7, 92.0, 70.3, 66.8, 21.3.

Reference

1. Das, M., Bandyopadhyay, D., Singh, R. P., Harde, H., Kumar, S., and Jain, S. Orthogonal biofunctionalization of magnetic nanoparticles via "clickable" poly (ethylene glycol) silanes: a "universal ligand" strategy to design stealth and

target-specific nanocarriers. *Journal of Materials Chemistry*, 22(47):24652-24667, 2012.