Chapter 5

A study on 2-methyl-1, 3-disulfoimidazolium polyoxometalate hybrid catalytic systems as safer alternative for sulfuric acid in nitration of aromatics

5A.1 Hybrid organic-inorganic polyoxometalates in catalysis

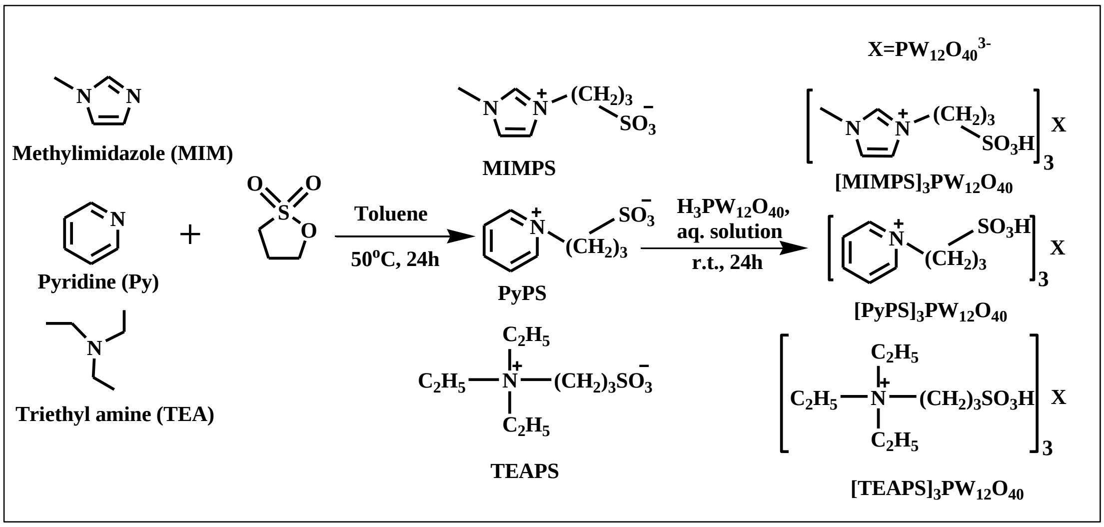
The first chapter of this thesis (**Chapter 1**, subunit **1.2.5**) briefly defined "polyoxometalates" as discrete anionic metal-oxygen clusters of interconnected {MOx} polyhedra containing M as transition metal cation of group V and VI elements in higher oxidation state, especially for $V^{+4/5}$, Mo^{+6} and $W^{+1/6}$ [1]. The presence of value added properties of polyoxometalates (POM) such as multi-electron redox reactions, Brönsted-acidic protons, tunable rigid structure, large sizes, high negative charges, nucleophilicity, good solubility in polar solvents *etc.* have been widely explored in various areas including catalysis, medicine, materials science, nanotechnology, molecular magnetism and photochemistry *etc.* [2-14]. Kasoulis *et al.* (1998) published one review article including collection of patent literature and uses of POM in different research areas other than catalysis and medicine [15]. The review ariticles published on the POMs have opened many scope to explore their potential uses in different directions [16-19].

The catalytic uses of POMs mainly concern with their super acidic nature and also excellent structural stability to undergo multi-electron redox cycles in homogeneous or heterogeneous catalysis, as photocatalysts or electrocatalysts. Large number of POMs involved in acid and oxidation catalysis [20-22]. Homogeneous POMs catalytic systems are preferable for several industrial scale catalytic processes because of highly efficient catalytic activity, low toxicity and less corrosive properties. However, the major problems of such POM catalysts are difficulties in recycling the catalyst and purification of product. Therefore, the designing of heterogeneous POM catalysts have received much attention from researcher to overcome the obvious drawbacks of homogeneous catalysis. Although immobilization of POMs on porous support develop efficient heterogeneous catalytic systems for many catalytic reactions, but the weak interaction between POMs and support lead to aggregation and leaching of POMs during catalysis as well as in work-up step. In this situation, the development of organic-inorganic hybrids of POMs have emerged as powerful route for creation of multifunctional POMs in combination with various organic components by covalent bond, electrostatic or other weak interactions that produce more efficient recyclable heterogeneous catalysts. Two types of organic-inorganic hybrids of POMs are found in literature [23]. Type-I material involves only electrostatic, H-bonds, or van der Waals interactions in between the organic and inorganic moieties, whereas type-II binds *via* strong covalent or iono-covalent bonds. The anionic nature of POM clusters allows strong association with organic counter cations in type-I hybrids.

Substitution of oxo group of the POMs by organic ligands directly links them to the metal center in type-II material. Linking of organic ligands may effectively form extended structure of the hybrid in various directions and dimensions through connection of metal ions. In this hybrid structures, the POMs moieties are uniformly distributed at molecular level and firmly anchored through covalent bonds or extensive H-bonds. The porosity and hydrophobicity of hybrid structure increases in presence of organic ligands and thus modifies the polarity of POMs framework [24]. The Brönsted and Lewis acidic sites of hybrids materials are associated with the POMs and the metal ions of the framework. Thus combining all their structural changes and newly added unique physical/chemical properties make the POMs water tolerant and recyclable heterogeneous catalysts. As a result, this concept of organic-inorganic hybrid of POMs have been employed to synthesize new class of task-specific ionic liquid based POM salts by pairing of anionic POM with or without functional group tethered organic cations [25]. The presence of Brönsted acidic functional groups (e.g.-COOH, -SO_3H) with the organic cation of hybrid POMs may provide more Brönsted-acidic character to these ionic salts. Additionally, hydrophobicity of the task-specific POMs salts can be changed through variation of chain length of alkyl substituents of the organic cations. These hybrid POMs ionic salts may work as efficient reusable heterogeneous catalysts for variety of oxidation and acid catalyzed organic reactions. The next subunit discusses the literature review of sulfonic acid functionalized POM ionic salts till 2017.

5A.2 SO_3H functionalized polyoxometalate ionic salts

A detailed literature search finds a number of –N-alkylsulfonic acid functionalized POM salts of imidazolium, ammonium and pyridinium cations as task-specific acidic ionic liquid materials along with catalytic uses in various organic reactions. Three members of solid organic-inorganic POM hybrid materials were prepared by Leng and his group (2009) and presented as $[MIMPS]_3PW_{12}O_{40}$, $[PyPS]_3PW_{12}O_{40}$, and $[TEAPS]_3PW_{12}O_{40}$ by combining propane sulfonate functionalized ionic liquid containing imidazolium, pyridinium and triethylammonium cations with Keggin-structured heteropolyanions (**Scheme 5A.1**). They investigated their catalytic activities [26] as “reaction-induced self-separation catalysts” for various esterification reactions with one of the reactants being polycarboxylic acid or polyol. The author also reported that these catalysts caused a liquid–liquid biphasic esterification system, presenting high yield and selectivity for target esters, and also quite easily recyclable for seven cycles [27].



Scheme 5A.1: Synthesis of heteropolyacid (HPA) salts

The pyridinium salt of polyoxometalate $[PyPS]_3PW_{12}O_{40}$ was again tested as effective catalyst for desulfurization of fuels in $[omim][PF_6]$ using aqueous H_2O_2 as oxidant by Huang *et al.* [28]. The catalysis procedure is simple, highly efficient and involves flexible recyclability. The desulfurization of fuel by the $–SO_3H$ functionalized imidazolium POM salt $[MIMPS]_3PW_{12}O_{40}$ was explored by Zhu and his coworkers (2011) along with three other POMs $[Bmim]_3PW_{12}O_{40}$ (1-butyl-3-methyl imidazolium phosphotungstate), $[Bmim]_3PMo_{12}O_{40}$ (1-butyl-3-methyl imidazolium phosphomolybdate) and $[Bmim]_4SiW_{12}O_{40}$ (1-butyl-3-methyl imidazolium silicotungstate). The reaction was completed in one hour at 30°C with S-removal of 100% and efficiently recycled up to 8th cycles with the same activity.

The optimized method of Leng *et al.* [26] for the preparation of -N alkyl sulfonic acid bearing POMs salts was utilized by Sun and his group for the synthesis of other similar members of imidazolium heteropolyacid ionic liquids $[C_4H_6N_2(CH_2)_3SO_3H]_{3-n}H_nPW_{12}O_{40}$ displayed in (**Fig.5A.1**). Their catalytic performances were studied successfully for one pot depolymerization of cellulose in to glucose, conversion of sucrose and starch into glucose and also one pot preparation of levulinic acid (LA) directly from cellulose [29]. They worked as easily separable catalysts without significant loss of catalytic activity.

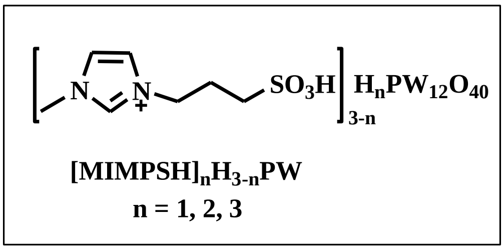
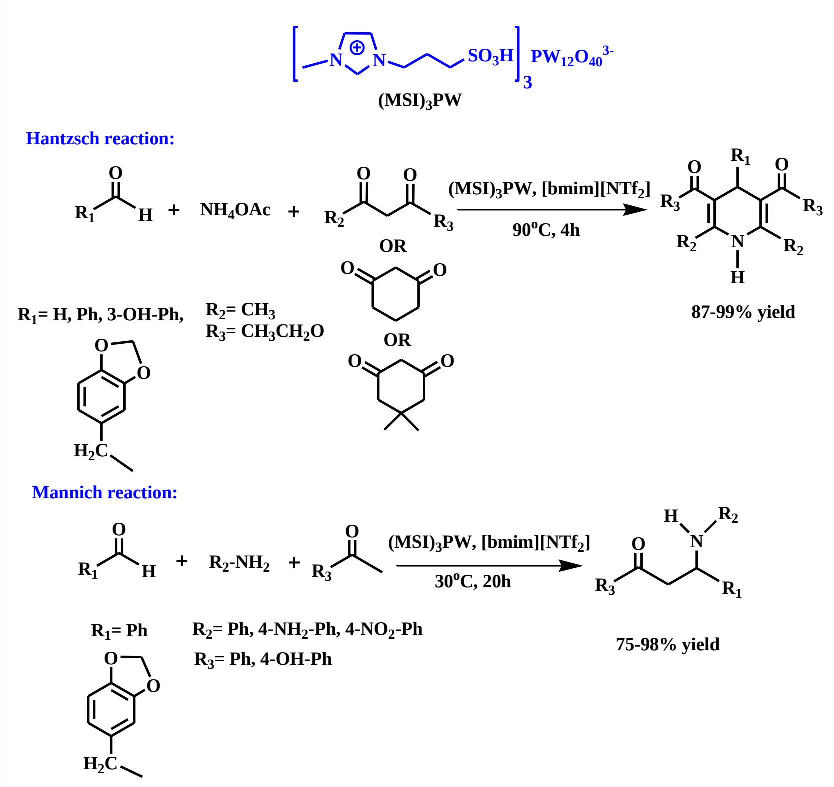
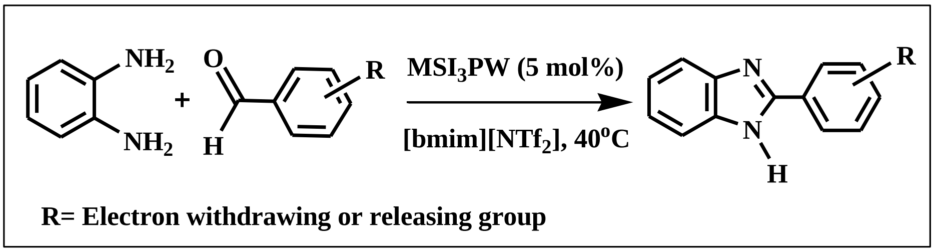


Fig.5A.1: Structure of $[MIMPSH]_nH_{3-n}PW$

In 2014, Alvim and his group [30] utilized (1-(3-sulfopropyl)-3-methylimidazolium phosphotungstate synthesized by Zhu *et al.* [31] as reusable catalyst in the three-component Mannich and Hantzsch reactions in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $[bmim][NTf_2]$.ionic liquid (**Scheme 5A.2**). They labeled this POM –ionic salt as $(MSI)_3PW$ instead of $[MIMPS]_3PW_{12}O_{40}$. The same author utilized this POM-IL in 2015 for condensation between aldehydes and *o*-phenylenediamines to afford 2-arylbenzimidazole derivatives (**Scheme 5A.3**) [32] using MSI_3PW (5 mol%) in $[bmim][NTf_2]$ ionic liquid at 40°C for 10 h to give 80-99% of products.



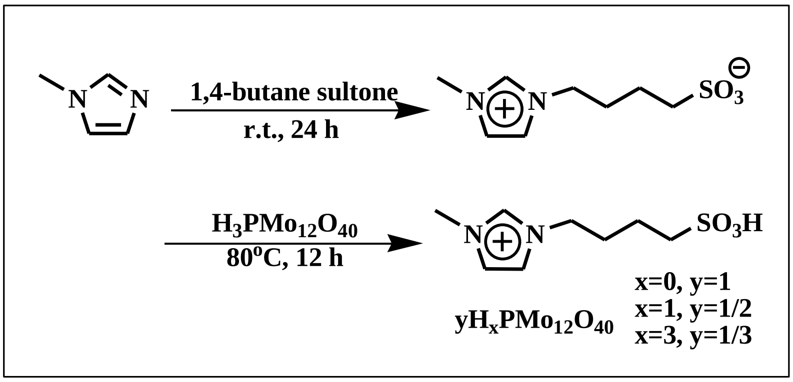
Scheme 5A.2: Three component Mannich and Hantzsch reactions catalyzed by $(MSI)_3PW$ supported in $[bmim][NTf_2]$ ionic liquid



Scheme 5A.3: Synthesis of 2-arylbenzimidazoles using MSI_3PW

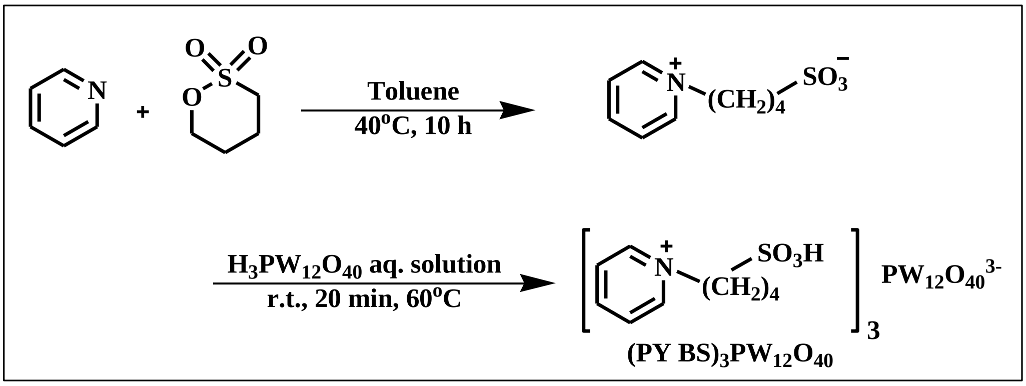
In 2013, Han *et al.* [33] fabricated polyoxometalate-based sulfonated ionic liquid catalysts by combining tungstophosphoric acid (TPA) and $-SO_3H$-functionalized zwitterions ionic complex 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS) to produce the POM salts abbreviated as $[MIM\text{-}PSH]_xH_{3-x}PW_{12}O_{40}$ in which x meant the molar ratio of MIM-PS/TPA changing from 1.0 to 3. Out of the five composite materials, namely $[MIM\text{-}PSH]_{3.0}PW_{12}O_{40}$, $[MIM\text{-}PSH]_{2.5}H_{0.5}PW_{12}O_{40}$, $[MIM\text{-}PSH]_{2.0}HPW_{12}O_{40}$, $[MIM\text{-}PSH]_{1.5}H_{1.5}PW_{12}O_{40}$, and $[MIM\text{-}PSH]H_{2.0}PW_{12}O_{40}$, the $[MIM\text{-}PSH]_{2.0}HPW_{12}O_{40}$ catalyst showed best catalytic performance with production of 90.4% of biodiesel from palmitic acid through esterification reaction. This catalyst could be recycled efficiently for six cycles under the optimized condition. This group also extended their same study for the preparation of pyridinium cation containing POM salts, [34] $[PPSH]_xH_{3-x}PW_{12}O_{40}$ (x = 1.0–3.0) by incorporating varied amounts of tungstophosphoric acid (TPA) and pyridinium propyl sulfobetaine (PPS) zwitterionic precursor according to the same method as Leng *et al.* in 2009 [26]. These self–separated catalytic systems were evaluated for acetalization of benzaldehyde with glycol which resulted in an optimal acetal yield over 85%.

Yang *et al.* [35] synthesized a series of Brönsted acidic Keggin structured POM ionic salts $[SO_3H(CH_2)_4Mim]_nH_{3-n}PMo_{12}O_{40}$ (n = 1, 2, 3) (**Scheme 5A.4**) and obtained their catalytic activity for regioselective mono nitration of aromatic compounds (e.g. toluene, benzene and chlorobemzene *etc.*) in HNO_3 (67%) for 10 hour at 70°C. The order of catalytic activity was obtained as $[(CH_2)_4SO_3HMim]_3PMo_{12}O_{40}$ > $[(CH_2)_4SO_3HMim]_2HPMo_{12}O_{40}$ > $[(CH_2)_4SO_3HMim]H_2PMo_{12}O_{40}$. The best catalyst $[(CH_2)_4SO_3HMim]_3PMo_{12}O_{40}$ was easily recycled and reused successfully for three consecutive cycles.

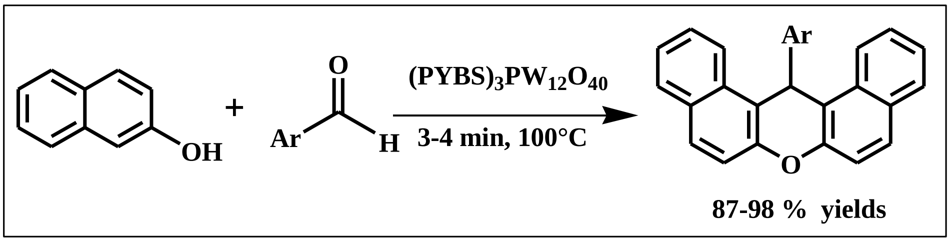


Scheme 5A.4: Synthesis of $[SO_3H(CH_2)_4Mim]_nH_{3-n}PMo_{12}O_{40}$ (n = 1, 2, 3)

Heravi *et al.* [36] introduced $-SO_3H$ functionalized POM ionic liquid of pyridinium cation and $PW_{12}O_{40}^{3-}$ Keggin anion (**Scheme 5A.5**) as reusable catalytic medium for preparation of 14-aryl-14*H* dibenzo[a, j]xanthenes at 100°C for 3-14 min reaction with excellent yields of the products (**Scheme 5A.6**). In 2012, Ebrahimi *et al.* further modified this POM-IL to a supported ionic liquid (IL) mediated sol–gel hybrid organic–inorganic material and presented for effective use in hollow fiber solid phase micro extraction (HF-SPME) [37].

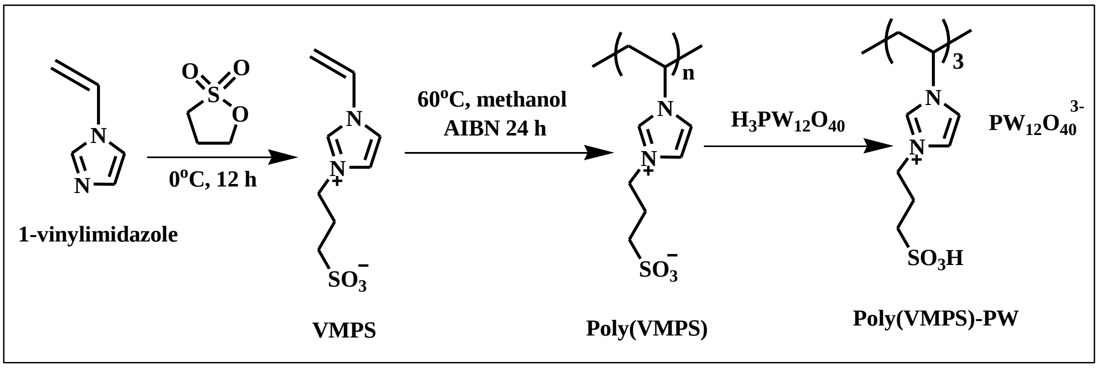


Scheme 5A.5: Synthesis of $(PYBS)_3PW_{12}O_{40}$



Scheme 5A.6: $(PYBS)_3PW_{12}O_{40}$ catalyzed synthesis of 14-aryl-14*H* dibenzo[a,j]xanthenes

Leng and his group (2012) continued to develop polymeric hybrid of -SO_3H-functionalized POM Brönsted acidic ionic salts from the reaction of $H_3PW_{12}O_{40}$ with polymeric 1-vinyl-3-propane sulfonate imidazolium [Poly(VMPS)] to yield the solid polymeric hybrid (**Scheme 5A.7**) [38]. The polymeric hybrid is highly active and selective solid catalyst for esterification under solvent-free conditions and can be easily recovered and steadily reused. Their stable and solid nature was accounted for the polymeric unit present in the frame.



Scheme 5A.7: Synthesis of Poly(VMPS)-PW

Zhen *et al.* (2012) synthesized $SiW_{12}O_{40}$-based ionic liquid (SWIL) (**Fig.5A.2**) and silica supported $SiW_{12}O_{40}$-based ionic liquid (SWIL/SiO_2) with different contents of SWIL [39]. They prepared two different compositions of SWIL/SiO_2 as per the reaction **Scheme 5A.8** involving reaction intermediates MPS-SiO_2-1 and MPS-SiO_2-2 by feeding the two weight ratios of silica to MPTMS ((3-mercaptopropyl) trimethoxysilane) such as 40:1 and 20:1, respectively. Both the ionic liquid systems SWIL and SWIL/SiO_2 showed better catalytic activity in esterification of oleic acid for biodiesel production. But the leaching of SWIL from silica support deactivated the SWIL/SiO_2 catalyst.

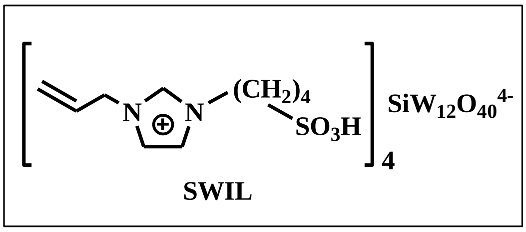
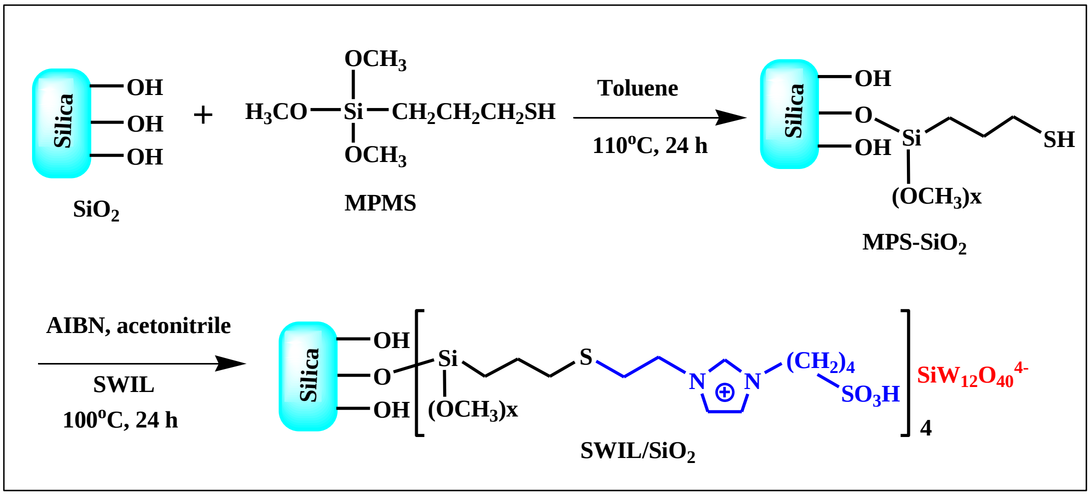


Fig.5A.2: Structure of SWIL



Scheme 5A.8: Synthesis of SWIL/SiO_2

Huang and his group (2014) [40] developed a series of homogeneous water-tolerable PPS-TPA-HOAc catalysts consisting of pyridinium propyl sulfobetaine (PPS), tungstophosphoric acid, and acetic acid and examined in catalytic acetylation of glycerol. These catalysts separated from glycerol acetate product as distinct liquid phase *via* self-segregate process after completion of the reaction.

Li *et al.* [41] prepared a series of self-separable POM salts of $[PyBS]^+$, $[TEABS]^+$ and $[MIMBS]^+$ cations pairing with $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ heteropolyacid anions (**Fig.5A.3**) and employed as reusable catalysts for (**Scheme 5A.9**) transesterification of trimethylolpropane (TMP). They also prepared [42] a series of Keggin and Dawson structured POM liquid catalysts consisting of $[PyBS]_n^+$, $[TEABS]_n^+$, $[ImBS]_n^+$ (n = 3, 4 and 5) cations and $H_2PV_2Mo_{10}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$, $P_2W_{18}O_{62}^{6-}$, $PV_2Mo_{10}O_{40}^{5-}$, $HPV_2Mo_{10}O_{40}^{4-}$, $SiW_{12}O_{40}^{4-}$, $PMo_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$ anions. They applied these multifunctional catalysts in one-pot transformation of cellobiose/cellulose to valuable chemicals, such as formic acid (FA) and levulinic acid (LA). Among them vanadium containing POM-IL catalyst is found to give a significantly higher selectivity of LA (46.3%) and FA (26.1%) than the other catalysts, together with 100% conversion of cellobiose.

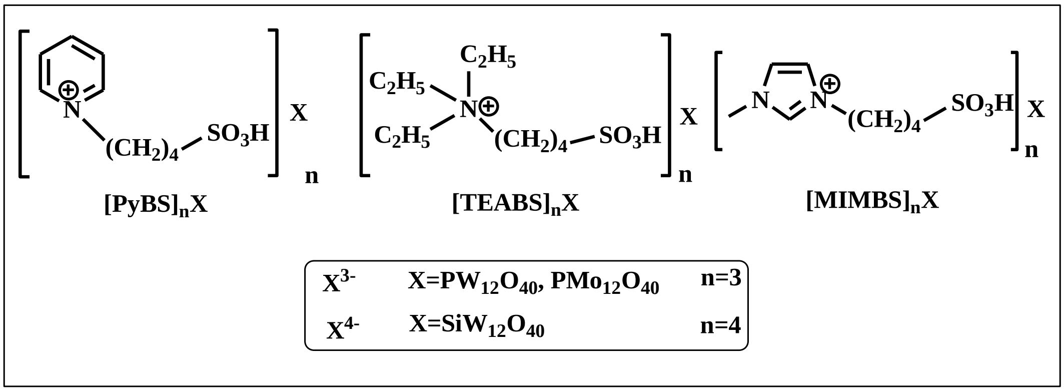
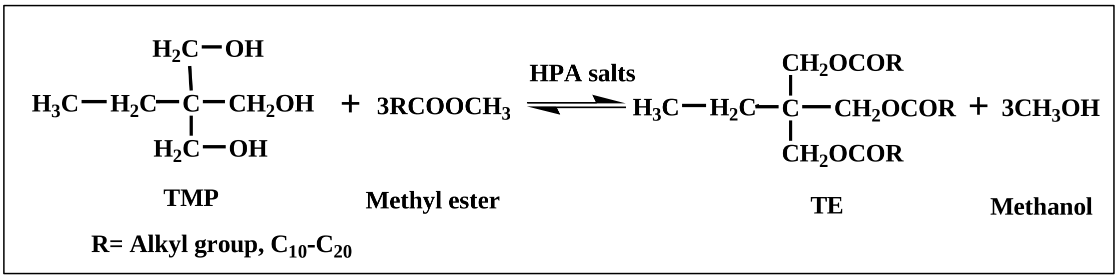


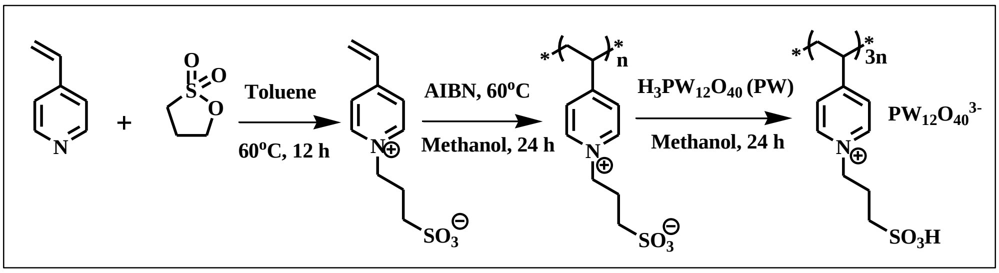
Fig.5A.3: Structures of heteropolyacid based ionic salts



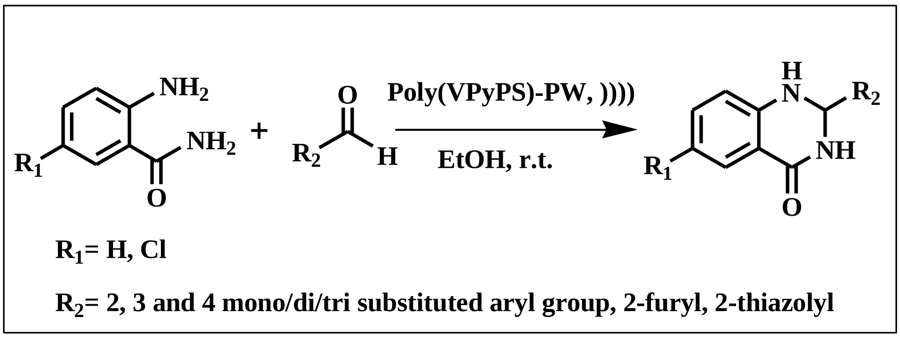
Scheme 5A.9: Transesterification of trimethylolpropane

Two of the above sulfonated imidazolium and ammonium based HPA-IL namely $[MIMBS]_3$ $PW_{12}O_{40}$ and $[TEABS]_nPW_{12}O_{40}$ showed excellent catalytic activity as studied by Liu *et al.* (2014) along with other HPA-ILs for the esterification reaction of diethylene glycolmonobutyl ether with acetic acid. They further studied their kinetic behavior [43].

Wang *et al.* developed another sulfonated poly(4-vinylpyridine) heteropolyacid salt poly(VPyPS)-PW (**Scheme 5A.10**) by the reaction of 4-vinylpyridine with 1, 3-propanesultone, followed by the polymerization and addition of the heteropolyacid [44]. This polymeric salt efficiently worked as reusable catalyst for synthesis of 2, 3-dihydro-4(1H)-quinazolinones derivatives under sonication irradiation (**Scheme 5A.11**).



Scheme 5A.10: Preparartion of poly(VPyPS)-PW



Scheme 5A.11: Poly(VPyPS)-PW catalyzed synthesis of 2,3-dihydroquinazolin-4(1H)-ones

Later on, they used this catalyst as reusable heterogeneous catalyst for one-pot synthesis of β-amino carbonyl compounds *via* Mannich reaction of aromatic aldehydes, aromatic ketones and aromatic amines in ethanol at room temperature [45].

Similar type of sulfonated heteropolyacid salt P(VB-VMS)PW was synthesized by anion-exchange of 1, 3-propanesulfonate poly(N-vinylimidazole-co-divinylbenzene) with Keggin structure of 12 phosphotungstic acid [46] (**Fig.5A.4**) and assessed their catalytic activity in Friedel-Crafts benzylation reaction between single-ring aromatic compounds with benzyl alcohol under solvent-free condition.

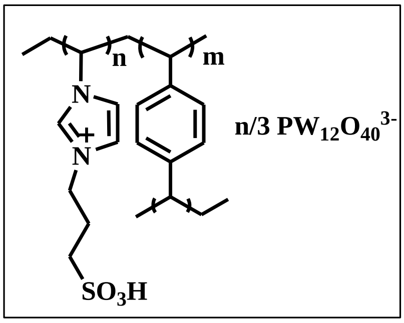
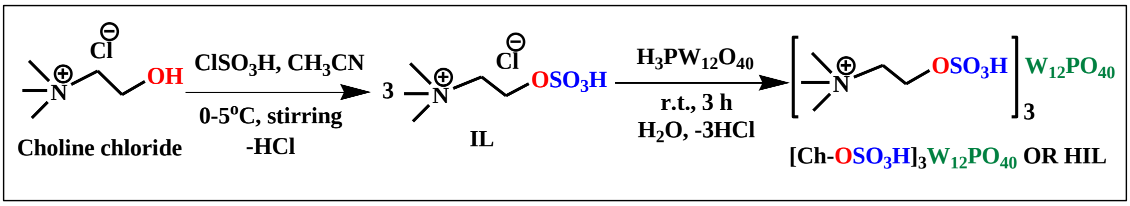


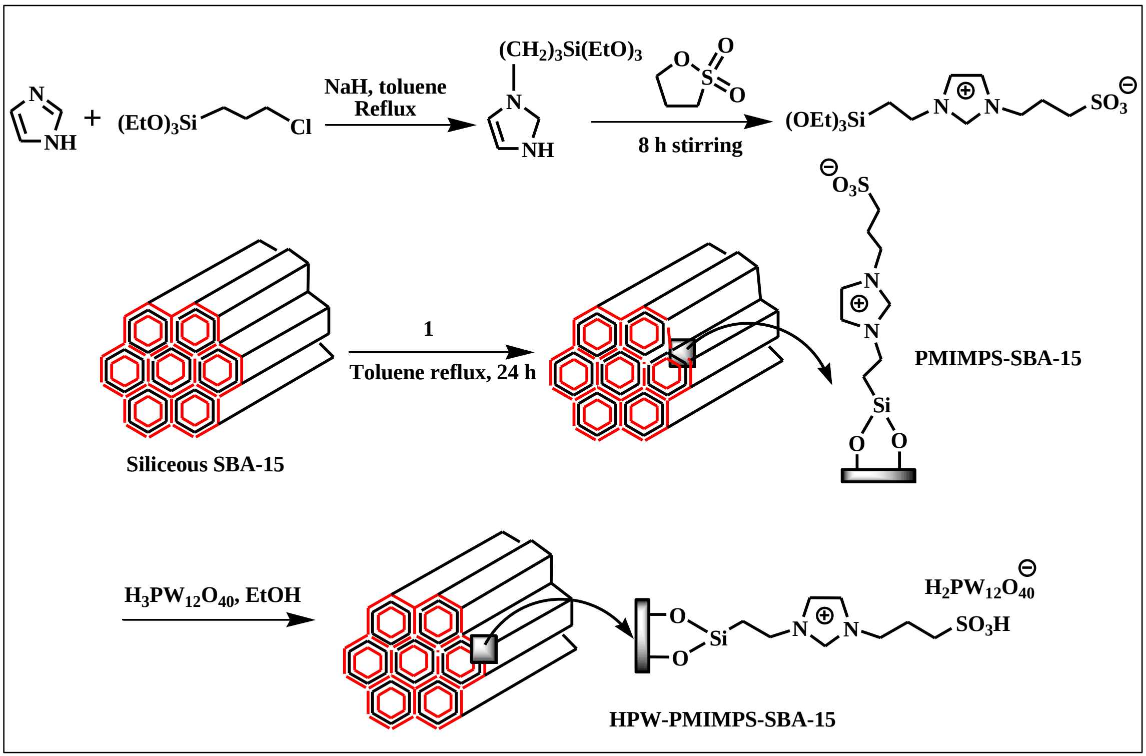
Fig.5A.4: Structure of P(VB-VMS)PW

Satasia and coworkers [47] prepared one heteropolyanion-based sulfated ionic liquid (HIL-$[Ch\text{-}OSO_3H]_3W_{12}PO_{40}$) by pairing sulfate functionalized cholinium cation [N, N, N-trimethyl-2-(sulfooxy)ethanaminium] with catalytically active phosphotungstic acid anion ($W_{12}PO_{40}^{3-}$) (**Scheme 5A.12**). The prepared ionic liquid was examined for N-formylation of amines under solvent-free grinding condition. This methodology provided cleaner conversion over 5-15 min reaction for primary and 40-95 min for secondary amines with high turnover frequency (TOF) and chemoselectivity.



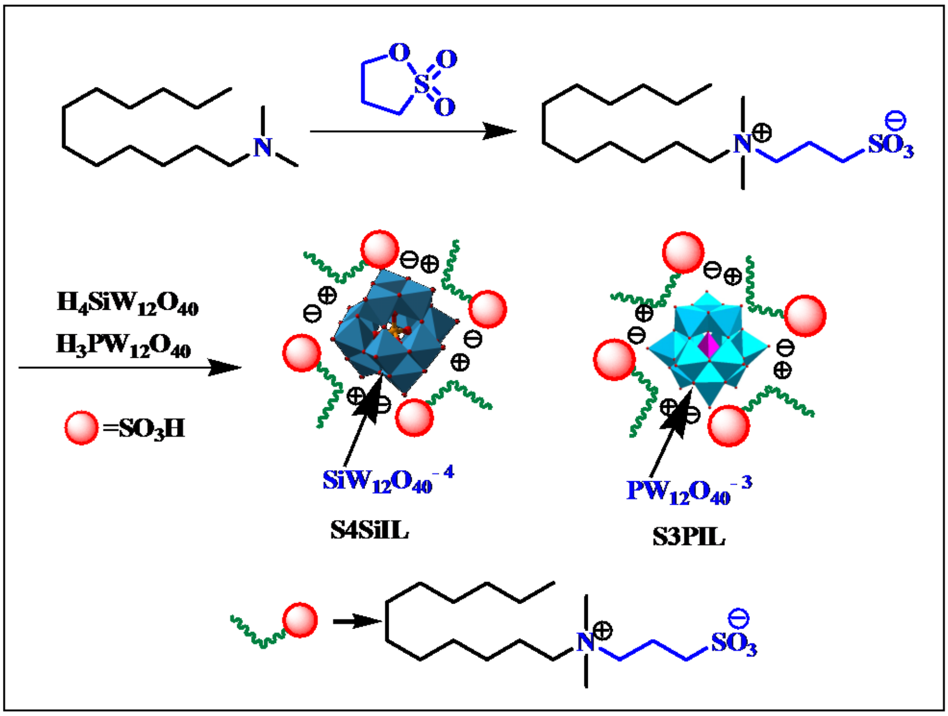
Scheme 5A.12: Synthesis of $[Ch-OSO_3H]_3W_{12}PO_{40}$

Sheng *et al.* [48] loaded various compositions of phosphotungstic acid ($H_3PW_{12}O_{40}$) on sulfonate-functionalized ionic liquid-modified mesoporous silica SBA-15 by total anion-exchange (HPW-PMIMPS-SBA-15) method (**Scheme 5A.13**). They concluded that the support material maintained its structure even after surface modification and the subsequent anion-exchange step of $[PW_{12}O_{40}]^{3-}$ (PW). The 30% HPW-PMIMPS-SBA-15 showed higher efficiency (97.8% styrene conversion with 93.9% yield of phenylxylyl ethane) in alkylation of o-xylene with styrene as compared to the task-specific basic ionic liquid (1-(propyl-3-sulfonate) 3-methyl-imidazolium phosphotungstate) (90.8% phenylxylyl ethane).



Scheme 5A.13: Synthesis of immobilized HPW-PMIMPS-SBA-15 materials

In 2015, Li *et al.* [49] introduced two long chain multi-SO_3H functionalized heteropolyanion-based ionic liquids S4SiIL and S3PIL (**Scheme 5A.14**). These two ionic liquids acted as efficient homogeneous catalysts in solvent free selective oxidation of alcohols with 35% aqueous hydrogen peroxide without adding any phase transfer catalyst. They can be recovered readily and reused efficiently for five times.



Scheme 5A.14: Synthesis of S4SiIL and S3PIL

The same group in 2015 [50] again developed three multi-SO_3H functionalized heteropolyanion-based ionic hybrids S2SiIH, S2PIH and S4SiIH (**Fig.5A.5**) using N, N, N′, N′-tetramethylethylene diamine or N, N, N′, N", N"-pentamethyldiethylenetriamine with 1, 3-propanesultone followed by addition of $H_4SiW_{12}O_{40}$ or $H_3PW_{12}O_{40}$. The obtained hybrids were used as recyclable heterogeneous catalysts for Baeyer–Villiger oxidation using 35% aqueous H_2O_2 as oxidant displayed high catalytic activity under solvent-free conditions.

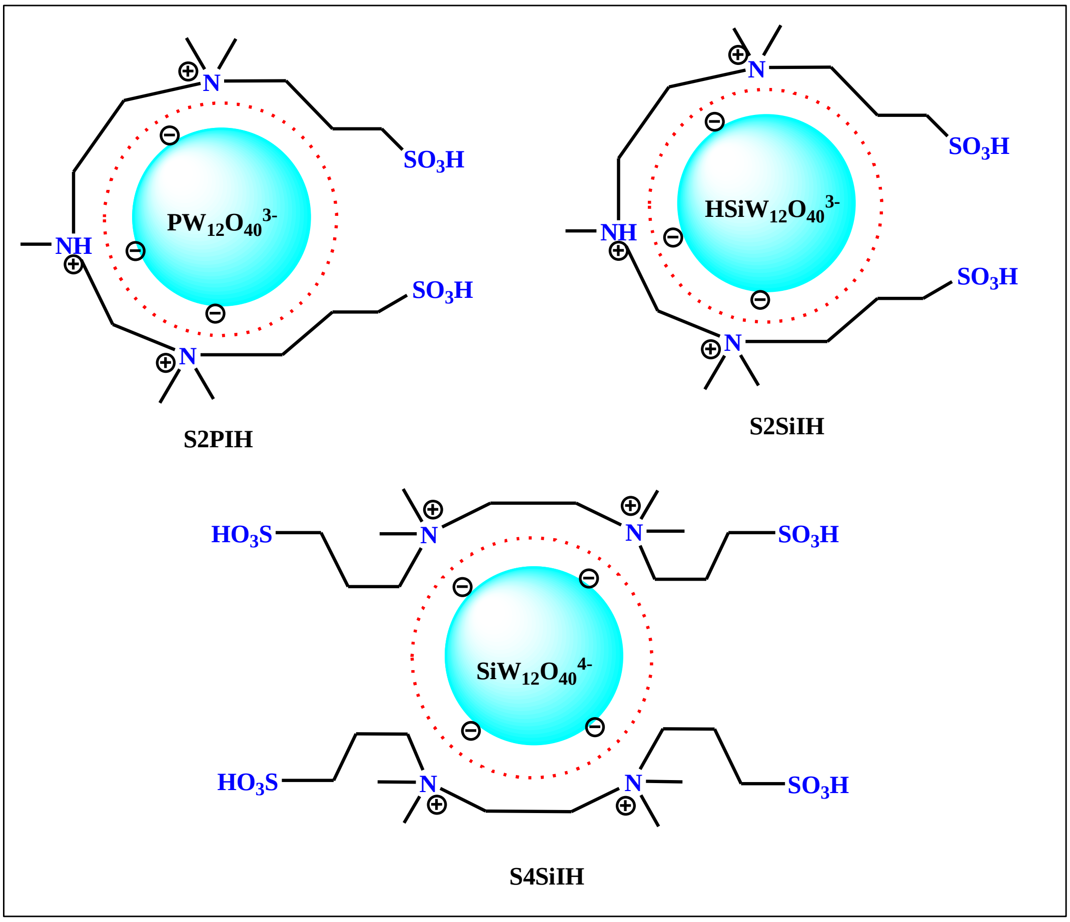
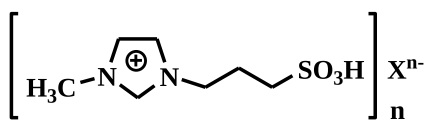


Fig.5A.5: Structures of heteropolyanion-based ionic hybrids S2SiIH, S2PIH and S4SiIH

Tong and his group [51] synthesized two POMs-based IL gels (**Fig.5A.6**) that exhibit typical thermotropic liquid-crystalline properties through grafting of two Keggin-type heteropoly anions such as $\{PMo_{11}VO_{40}\}^{4-}$ and $\{PW_{11}MoO_{40}\}^{3-}$ by using N-methyl imidazolium-1-(3-sulfonic group) propyl (MIMPS) ionic liquid. They studied their electrochemical stability, ionic conductivity and compared with various known IL-based electrolytes. The gel electrolytes showed higher electrochemical stability as well as conductivity.



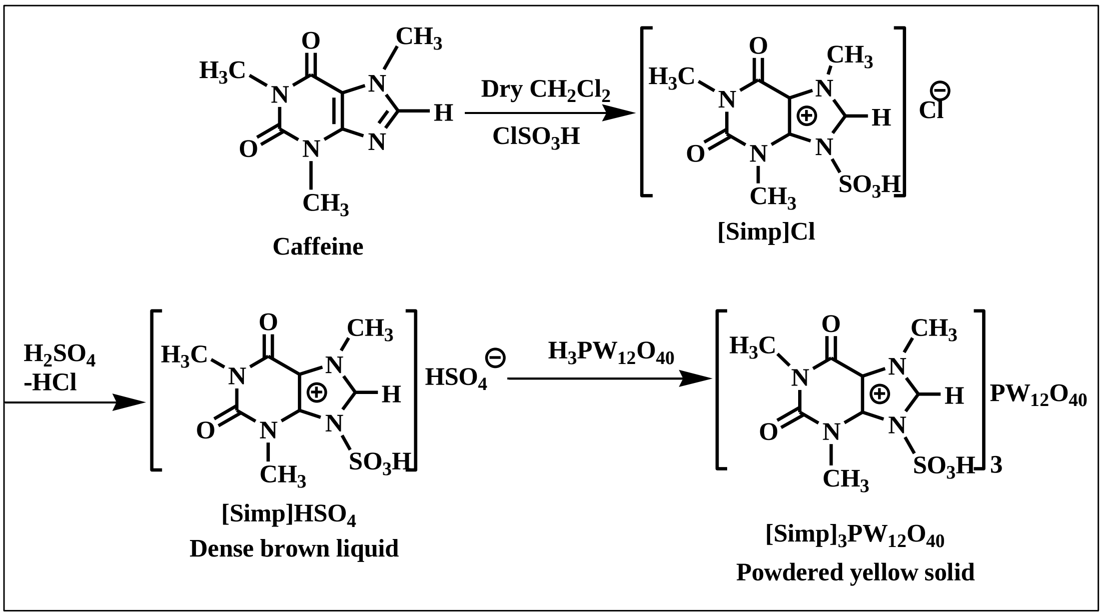
n=3, X=PW$_{11}$MoO$_{40}$$^{3-}$, (IL-PW$_{11}$Mo)

n=4, X=PMo$_{11}$VO$_{40}$$^{4-}$, (IL-PMo$_{11}$V)

Fig.5A.6: Structures of gel electrolyte POM

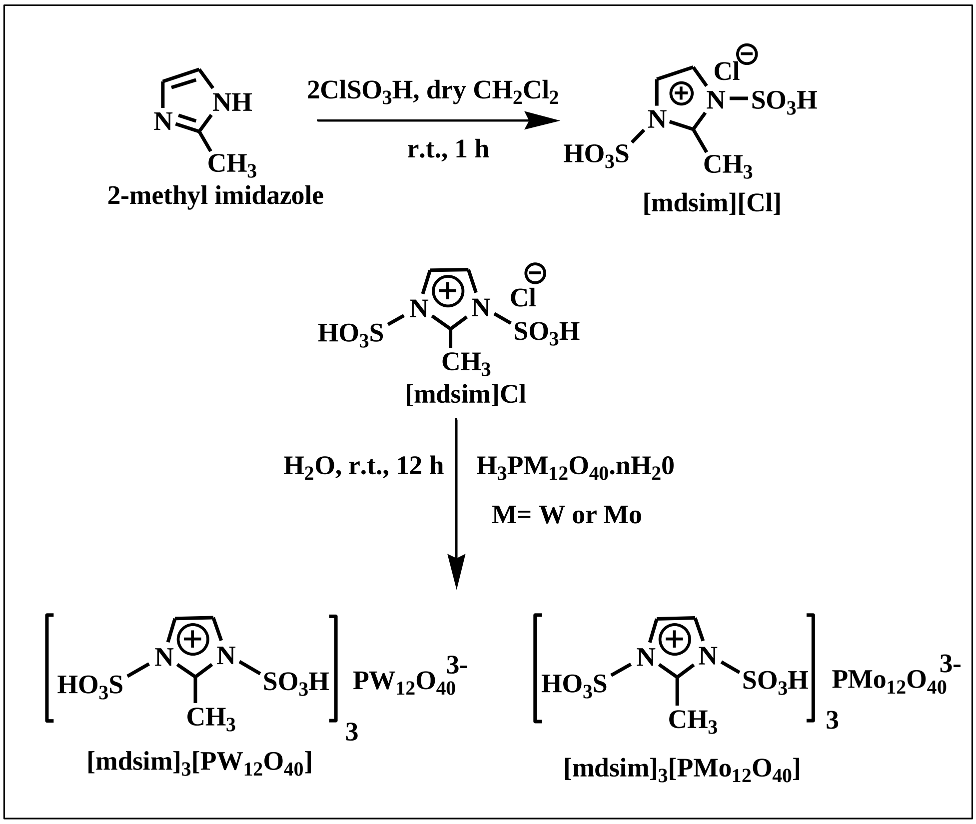
Han *et al.* [52] reported a series of Keggin-type HPA-based ionic liquid catalysts ($[MIM\text{-}PSH]_xH_{4-x}PVMo_{11}O_{40}$, x = 1-4) synthesized from the zwitterion 3-(1-methylimidazolium-3-yl)propane-1-sulfonate ionic liquid (MIM-PS) and molybdovanadophosphoric acid ($H_4PVMo_{11}O_{40}$). Their catalytic activities were evaluated in esterification of n-caprylic acid to methylcaprylate, among which the $[MIM\text{-}PSH]_{2.0}H_{2.0}PVMo_{11}O_{40}$ catalyst showed an optimal reaction activity.

Recently, Tayebee *et al.* developed heteropolyacid-based ionic liquid $[Simp]_3PW_{12}O_{40}$ from the reaction of 3-sulfonic acid 1-imidazolopyridinium hydrogen sulfate $[Simp]HSO_4$ with $H_3PW_{12}O_{40}$ in aqueous solution and then transformed into nano-form *via* solvothermal processing in tetralin at 220°C (**Scheme 5A.15**) [53]. This was applied as heterogeneous nanocatalyst in one-pot, multi-component reaction of aldehydes, phthalhydrazide and dimedone under solvent free condition at 100°C to give 2H-indazolo[2, 1-b]phthalazine-1, 6, 11(13H)-trione within short time.



Scheme 5A.15: Synthesis of $[Simp]_3PW_{12}O_{40}$

This literature search shows that all these acidic POM-ionic salts were made up of various organic cations attached only with –N alkyl sulfonic group for which they expressed strong Brönsted –acidic nature and also isolated in solid or liquid state depending on their melting point temperatures. No reports are found for the synthesis of direct $-N\text{-}SO_3H$ functionalized POMs ionic salts of imidazolium, ammonium or pyridinium cations. Therefore, **Section 5B** of this chapter discusses the preparation, characterization and catalytic uses of direct N-SO_3H functionalized 1, 3-disulfoimidazolium POM-salts of phosphotungstic acid and phosphomolybedic acid as reusable heterogeneous catalysts for nitration of aromatic hydrocarbons at ambient temperature within short time (**Scheme 5A.16**).



Scheme 5A.16: Synthesis of N-SO_3H functionalized 1, 3-disulfoimidazolium POM-salts $[mdsim]_3[PW_{12}O_{40}]$ and $[mdsim]_3[PMo_{12}O_{40}]$

5A.3 Nitration of aromatic compounds involving ionic liquid systems

Nitration reaction is widely used in chemical industry as unit process for synthesis of nitro-aromatic compounds which are also extensively applicable as chemical feedstock of large number of essential chemical products such as dyes, perfumes, pharmaceutical, fertilizers, plastics, and explosives [54, 55]. The nitro-aromatics are again utilized as reaction intermediate for functional group transformation reactions [56-58]. A large number of reagents and catalysts have been developed to avoid release of excess acid waste stream, use of excessive reagents, over nitration, oxidative side products and safety problems of common nitrating agents involving mixtures of concentrated or fuming HNO_3 with H_2SO_4 acids [59-61].

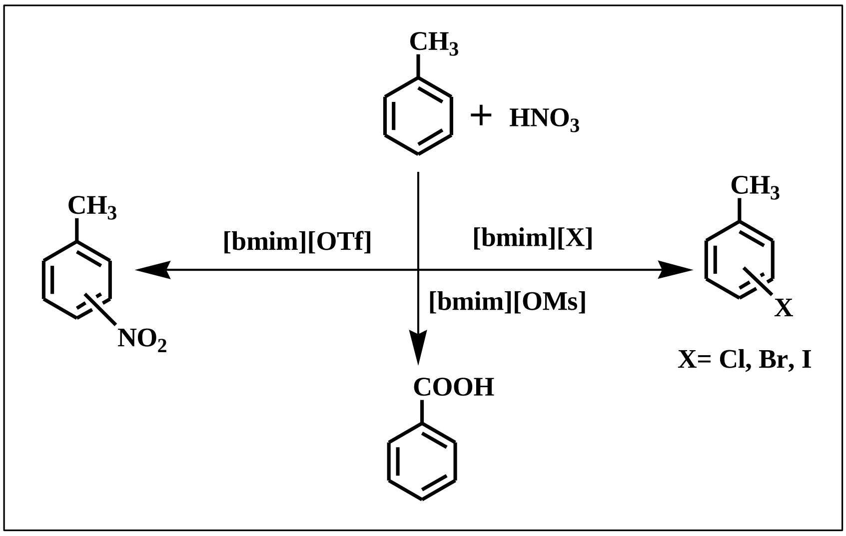
These modified strategies involved the use of superacids, alkyl nitrates, nitronium salts or metal nitrates [57, 62-66], ionic liquids [59, 60], supported catalysts [67, 68]. Some examples of modified nitrating systems are silica sulfuric acid/$NaNO_2$/wet SiO_2 [69], HNO_3/mixed metal oxides [70], HNO_3/lanthanide reagents [71], HNO_3-Ac_2O in [bmpy][$N(Tf)_2$] [72], N-nitropyridinium salts [73], trimethyl silyl nitrate [74], HNO_3 in [bmim][OTf] [75] *etc.*

Laali and his coworkers [76] utilized a series of 1-ethyl-3-methylimidazolium salts [emim][X] (X = OTf^-, CF_3COO^-, and NO_3^-) and [$HNEtPri_2$][CF_3COO] ionic liquids as solvents for electrophilic nitration of aromatics using a variety of nitrating systems including NH_4NO_3/TFAA, isoamyl nitrate/$BF_3.Et_2O$, isoamyl nitrate/TfOH, $Cu(NO_3)$/TFAA and $AgNO_3$/Tf_2O. Out of these, NH_4NO_3/TFAA with [emim][CF_3COO], [emim][NO_3] and isoamyl nitrate/$BF_3.Et_2O$, isoamyl nitrate/TfOH with [emim][OTf] displayed the best performances in terms of product yields and recycling/reuse of the ionic liquids. These studies showed that the yields and selectivity of nitration products strongly depended on the substrate structure.

Highly regioselective *p*-nitro product was prepared by Rajagopal *et al.* (2003) from phenols using $Fe(NO_3)_3$ in ionic liquid solvent 1, 3-di-*n*-butylimidazolium tetrafluoroborate [bbim][BF_4] within 1-3 hour at 30-60°C [77].

Lancaster and his co-worker in 2003 [72] studied the importance of cation choice for ionic liquid as solvent during nitration of aromatics using HNO_3-Ac_2O as nitrating agent. They observed that aromatic substrates can be nitrated efficiently under mild condition with the HNO_3-Ac_2O in [bmpy][$N(Tf)_2$] where [bmpy] represents N-butyl-N-methylpyrrolidinium cation which is relatively inert to nitration in contrast to 1-butyl-3-methylimidazolium cation containing ionic liquids [bmim][BF_4] and [bmim][$N(Tf)_2$].

In 2004 Earle *et al.* [75] demonstrated that the reaction of toluene and 67% nitric acid in three different ionic liquids as shown in **Scheme 5A.17** gives rise to three completely different products in high yields with very little cross contamination.



Scheme 5A.17: Reaction of toluene and 67% nitric acid in three different ionic liquids

It was observed that only 10 mol% of [bmim][OTf] acted as efficient nitration catalyst with various aromatic compounds in presence of 67% nitric acid. They also screened a series of ionic liquids for the same reaction which include [$C_n$mim][X] (n = 10, 12; X = OTf, Cl, Br), [bmim][X], (X = OTf, OMs, NO_3), [emim][HSO_4], [NBu_4]I ionic liquids.

Powell *et al.* [78] investigated the nitration of arenes in tetraalkylphosphonium ionic liquids (**Fig.5A.7**) as solvents and compared their results with the reports of Lancaster [72]. The author found that the phosphonium based ionic liquids are effective solvents under mild nitration of various arenes and offer many advantages as compared to N, N-dialkylimidazolium ionic liquids.

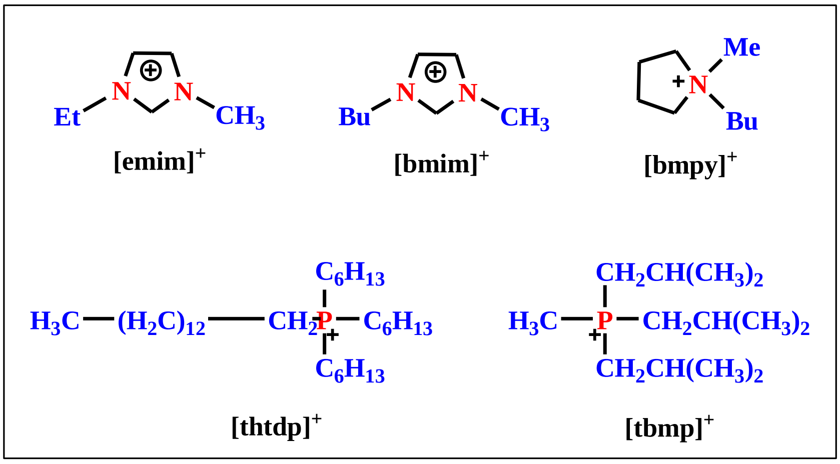


Fig.5A.7: Structures of general cations

Lancaster and his coworkers in 2005 [79] examined the nitration of a range of activated and deactivated aromatic substrates by acetyl nitrate in two ionic liquids [bmpy][N(Tf)$_2$] and [bmpy][OTf] (**Fig.5A.8**). They developed a method in which [bmpy][N(Tf)$_2$] can be recovered and reused for aromatic nitration.

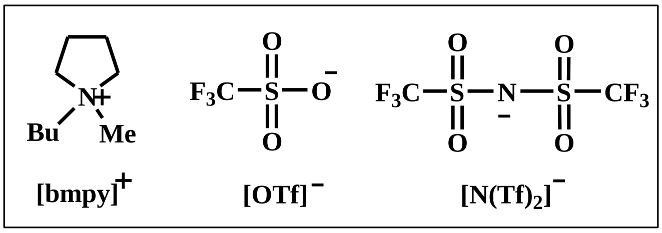


Fig.5A.8: Cation and anions of the two ionic liquids

Smith *et al.* utilized [80] three air and moisture stable ionic liquids [bmim][BF$_4$], [bmim][PF$_6$] and 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate [bdmim][BF$_4$] for regioselective mononitration of simple aromatic compounds under mild conditions (HNO$_3$ and acetic anhydride) which was compared with the results reported by Lancaster [72].

In 2008, Qi *et al.* [81] employed Brönsted acidic ILs [Caprolactam]X (X = p-TSO$^-$, BSO$^-$, BF$_4^-$, NO$_3^-$) (**Fig.5A.9**) as recyclable medium for the nitration of simple aromatics with NO$_2$/air catalytic system at atmospheric condition in absence of any organic solvent.

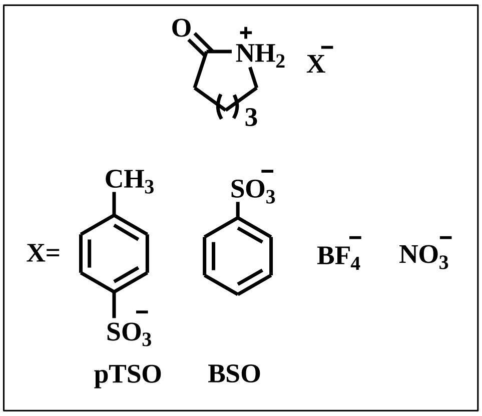


Fig.5A.9: Structure of caprolactum based ionic liquids

Wang and his coworkers [82] performed nitration of substituted benzenes efficiently in catalytic amount of Cu(N(C$_4$F$_9$SO$_2$)$_2$)$_2$/[N$_{4446}$][Tf$_2$N] or In(NTf$_2$)$_3$/[N$_{4446}$][Tf$_2$N] ionic liquids using HNO$_3$/Ac$_2$O as nitrating agents and achieved 81.4-90.3% conversion in presence of $Cu(N(C_4F_9SO_2)_2)_2$/[N_{4446}][Tf_2N]. The same group reported [83] lanthanide bis[(trifluoromethyl)sulfonyl]-imides as a kind of effective catalyst in quaternary ammonium ionic liquids for the nitration of substituted benzenes with concentrated nitric acid (95%) (**Fig.5A.10**). In both cases, the catalytic systems with ionic liquids could be easily recovered and reused for five runs.

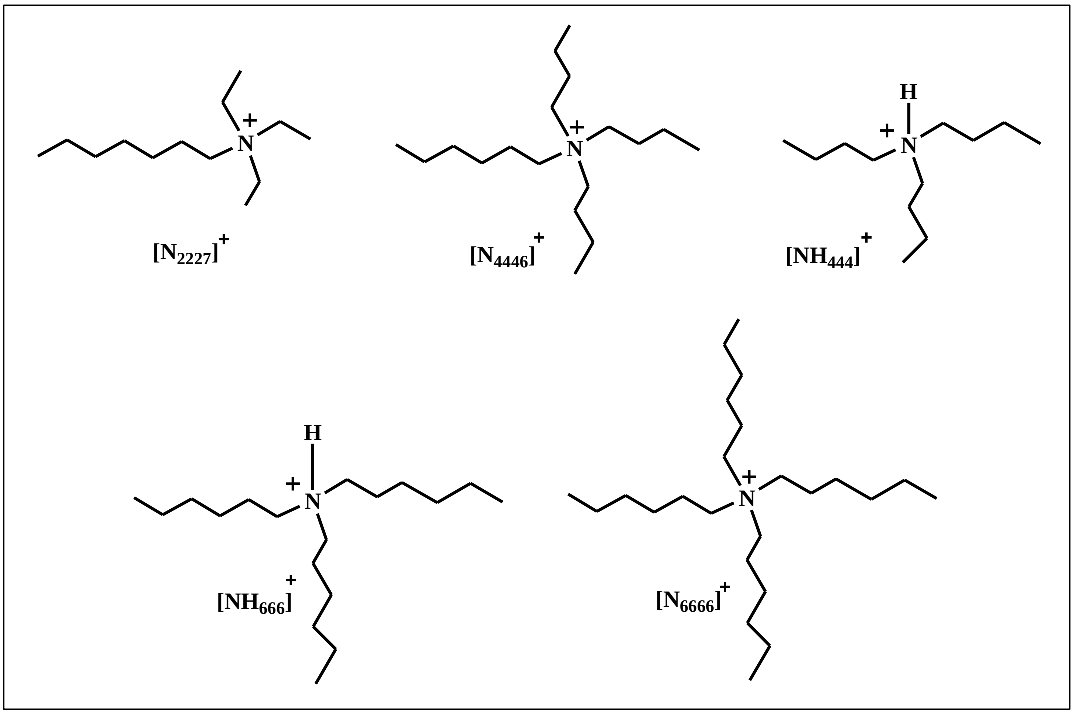


Fig.5A.10: Structures of quaternary ammonium cations used by Wang *et al.*

Acidic ionic liquid [bmim][HSO_4] (**Fig.5A.11**) was used by Tajik and his group for selective nitration of phenols with sodium nitrate [84].

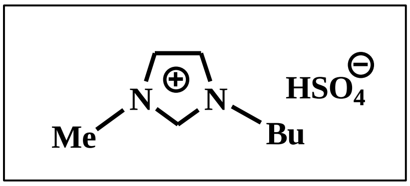
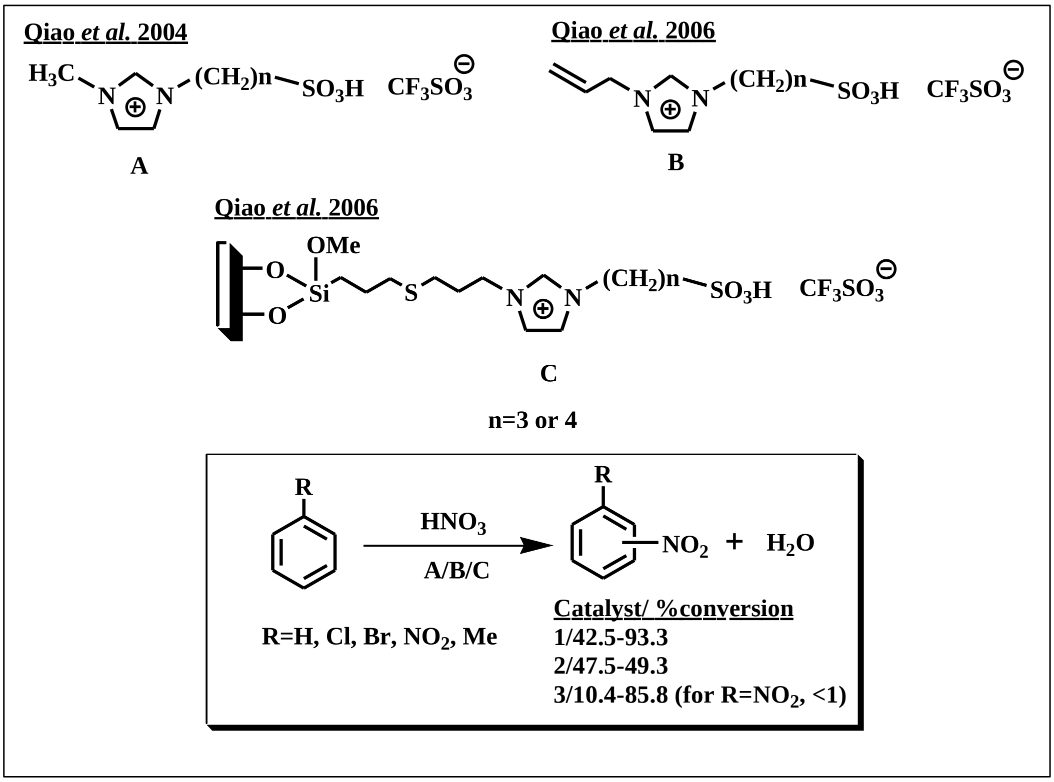


Fig.5A.11: Structure of [bmim][HSO_4] ionic liquid

Aridoss *et al.* in 2011, [85] employed EAN/Tf_2O and EAN/TFAA (EAN = ethyl ammonium nitrate) systems as convenient *in situ* sources of triflyl nitrate ($TfONO_2$) and trifluoroacetyl nitrate (CF_3COONO_2) for facile nitration of a wide range of aromatics including strongly deactivated systems under very mild conditions, in respectable yields, and in a simple operation, with recovery and reuse of the IL.

A suspension of $Bi(NO_3)_3.5H_2O$ (BN) in imidazolium ionic liquids [bmim][PF_6] or [bmim][BF_4] was used as an effective nitrating reagent for ring nitration of activated aromatics under mild conditions by Jacoway and his group [86].

Besides the above mentioned ionic liquids, there has been trending another group of task specific $–SO_3H$ functionalized Brönsted acidic ionic liquids based on various organic cations. Main role of such ionic liquids is to minimize the harmful use of H_2SO_4 in nitration reactions. Qiao and Yokoyama introduced a solvent free method for nitration of simple aromatic compounds with 62% nitric acid in presence of 3-methyl-1-(4-sulfobutyl) imidazolium trifluoromethanesulfonate or 3-methyl-1-(3-sulfopropyl) imidazolium trifluoromethanesulfonate as reusable catalysts [87]. The same group again developed 1-allylimidazoium ionic liquid immobilized 3-mercaptopropyltrimethoxysilane (MPS) modified silica gel as heterogeneous catalyst for esterification and nitration reactions [88] (**Scheme 5A.18**).



Scheme 5A.18: Brönsted acidic ionic liquid catalyzed nitration by Qiao *et al.*

A series of Brönsted acidic ionic liquids reported by Cheng *et al.* in 2008 (**Fig.5A.12**) were utilized as catalyst in nitration of aromatic compounds with NO_2/air under solvent free condition [89]. They afforded mono-nitration products and *para* selectivity with better reusability. However, percentage yields are not satisfactory. In the same year Fang and his coworkers developed some halogen free acyclic Brönsted acidic task-specific ionic liquids (TSILs) that bear an alkane sulfonic acid group in an acyclic trialkanylammonium cation (**Fig.5A.13**) and used as catalysts for regioselective mononitration of aromatic compounds at 60-80^{o}C [90]. Yields were reasonable with improved *para* selectivity.

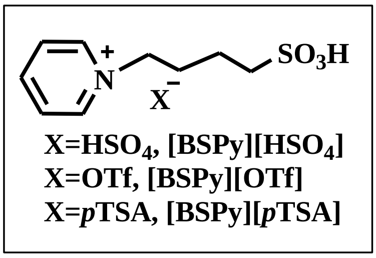


Fig.5A.12: Structure of –SO_3H functionalized ionic liquids

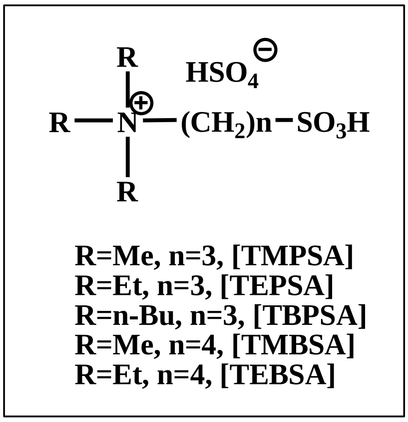
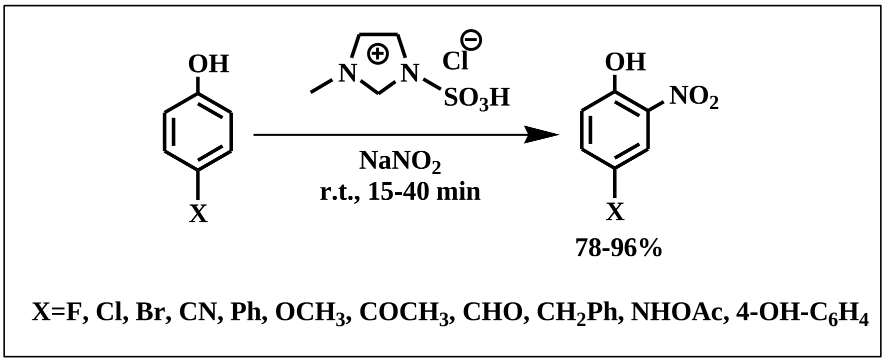


Fig.5A.13: Structures of trialkanylammonium based sulfonic acid functionalized IL

Khazei *et al.* reported [91] nitrosation-oxidation of phenols by 3-methyl-1-sulfonic acid imidazolium chloride [Msim][Cl] as a new Brönsted acidic ionic liquid and $NaNO_2$ at room temperature (**Scheme 5A.19**).



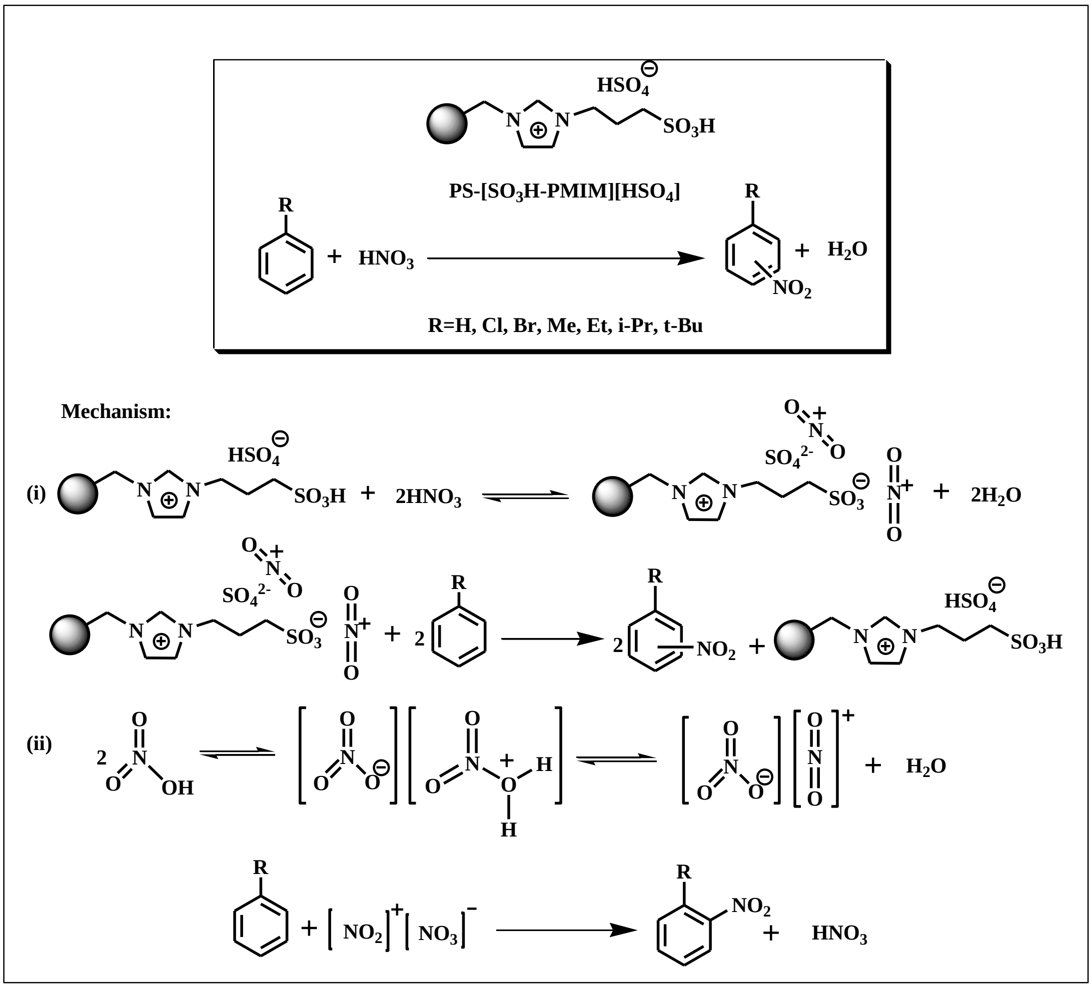
Scheme 5A.19: Mononitration of phenols using [Msim][Cl]

The first Keggin structured POM Brönsted acidic salts (KHBISs) $[SO_3H(CH_2)_4Mim]_{3n}H_{3n}PMo_{12}O_{40}$ (n = 1, 2, 3) (**Scheme 5A.4**) was utilized as reusable catalyst in aromatic nitration by Yang *et al.* in the year 2011 [35].

In 2012, Li and his group [92] developed a series of polystyrene-supported 1-(propyl-3-sulfonate)-3-methyl-imidazolium hydrosulfate acidic ionic liquid (PS-[SO_3H PMIM][HSO_4]) catalysts and tested for mononitration of simple aromatics compounds with nitric acid. The reactivity of the catalysts increased with increasing [SO_3HPMIM][HSO_4] content. The authors proposed a reaction mechanism for this ionic liquid assisted nitration of aromatics (**Scheme 5A.20**).

In the same year Zolfigol and his coworkers introduced 3-Methyl-1-sulfonic acid imidazolium nitrate ([Msim]-NO_3) as a new Brönsted acidic ionic liquid and nitrating agent for the efficient nitration of aromatic compounds (even aniline derivatives) by *in situ* generation of nitrogen dioxide (**Fig.5A.14**) [93]. Nitration of various aromatics was completed within very short time of 1-2 min giving good to excellent yields (45-95%).

The same work was extended by Zare *et al.* using 1-sulfopyridinium nitrate [pyridine–SO_3H][NO_3] and utilized as outstanding nitrating agent for nitration of arenes (**Fig.5A.15**) [94]. They also proposed *in situ* generated nitrogen dioxide as a radical source for the presented nitration protocol.



Scheme 5A.20: Mechanism of aromatic nitration catalyzed by PS-[SO_3H PMIM][HSO_4]

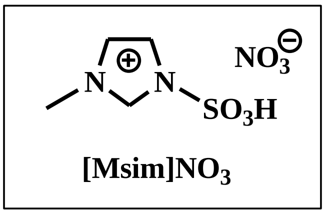


Fig.5A.14: Structure of [Msim]-NO_3

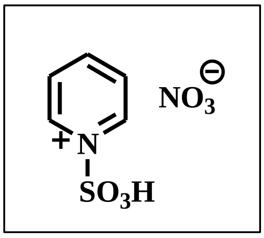


Fig.5A.15: Structure of [pyridine–SO_3H][NO_3]

Thus, ionic liquids excellently serve the purpose of solvents, catalysts and nitrating agents without using the conventional acids. For this purpose, we aimed to investigate the catalytic efficacy of 2-methyl-1, 3-disulfoimidazolium polyoxometalate hybrid salts (**Scheme 5A.16**) as reusable heterogeneous catalysts for nitration of aromatic compounds at room temperature/heat stirring using 69% HNO_3 acid which are included in **Section 5B** of this chapter.

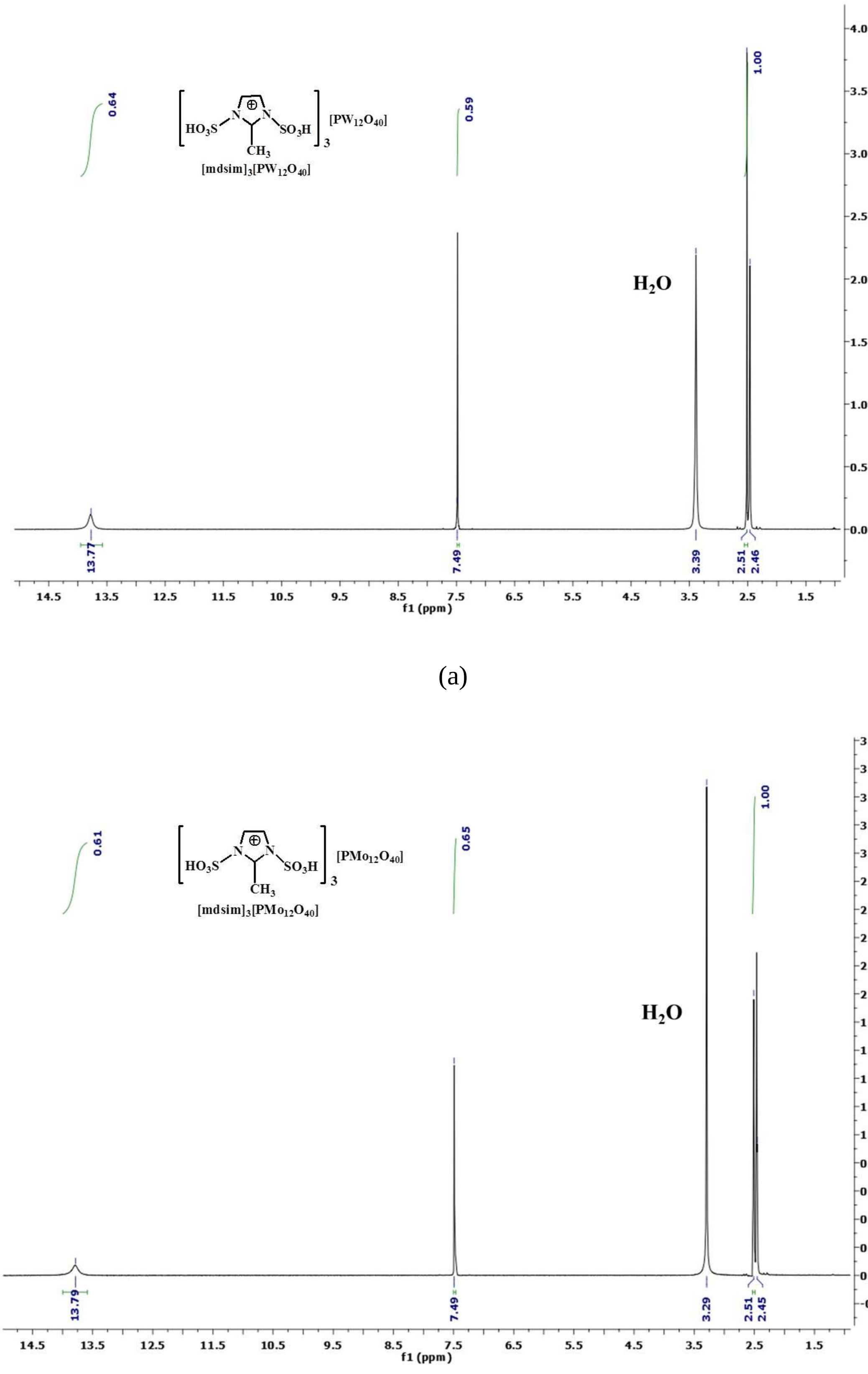
5B.1 Synthesis and characterization of organic-inorganic hybrid polyoxometalates

The formation of -SO_3H functionalized 2-methylimidazolium polyoxometalates (POMs) of phosphotungstate and phosphomolybdate $[mdsim]_3[PM_{12}O_{40}]$ (where M = W & Mo) were achieved by following a two step method (**Scheme 5A.16**, **Section 5A**) as described in experimental section (subunit **5B.4**). The two solid POM salts were subjected to various analytical techniques to complete their structural, thermal and Brönsted-acidic characterization process. Herein, the inherent Brönsted acidic properties of -SO_3H group of these POM salts were studied for nitration of aromatic compounds with 69% HNO_3 at normal temperature and 80°C without use of any external concentrated sulfuric acid.

NMR analysis

Analysis of ^1H NMR spectra of both the hybrid compounds in DMSO-d_6 displayed one singlet of two protons at 13.77-13.79 ppm for the -SO_3H groups of imidazolium cation (**Fig.5B.1**). Their ^{13}C NMR spectra also evidenced the existence of imidazolium ring carbons within the structures of hybrid material (**Fig.5B.2**). ^{31}P NMR spectra of the heteropolyacids (HPAs) and the hybrid compounds of POMs were showed in Fig.**5B.3a** and **Fig.5B.3b**. The phosphorus peak of phosphotungstic acid at -14.98 ppm is changed to -15.25 ppm for the $[mdsim]_3[PW_{12}O_{40}]$. The same peak of phosphomolybdic acid at -3.47 ppm is shifted to -3.94 ppm for the $[mdsim]_3[PMo_{12}O_{40}]$. The characteristic sharp and symmetric resonance peaks of phosphorus in tetrahedral position of the Keggin structured anions in each of the HPA are slightly moved towards higher frequencies in case of the hybrid compounds and thus indicate strong ionic interaction between the imidazolium cation and Keggin anion of the hybrid compounds. The up field resonance of ^{31}P signals signifies the retention of heteropolyanions with a small hydration sphere observed from dynamic dehydration equilibrium involving dioxonium group $H_5O_2^+$ (**Equation 5B.1**) as proposed to explain the behavior of hydration environment as a function of temperature close to room temperature using NMR study [95, 96].

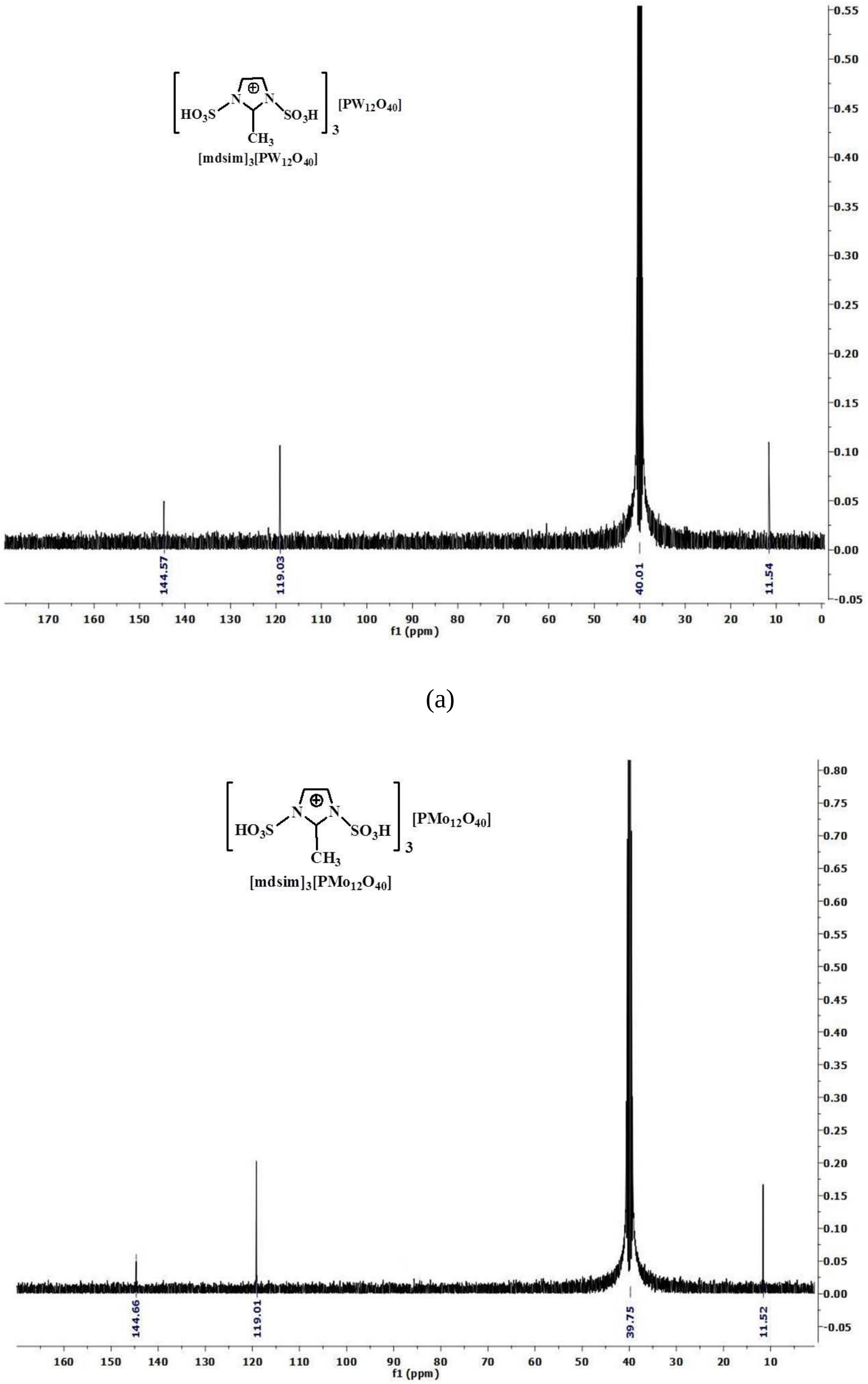
$$\mathbf{H_5O_2^+ \longleftrightarrow H_3O^+ + H_2O \longleftrightarrow H^+ + 2H_2O} \qquad \text{(Equation 5B.1)}$$



(a)

(b)

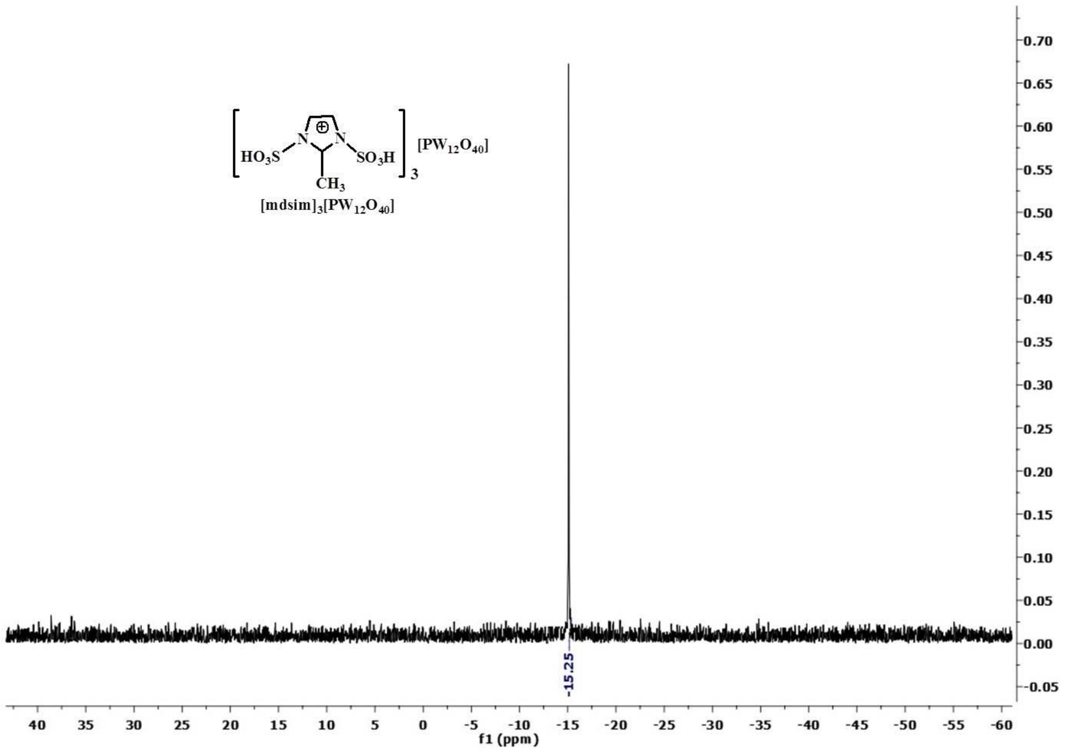
Fig.5B.1: ^{1}H NMR spectra of (a) [mdsim]$_3$[PW$_{12}$O$_{40}$] & (b) [mdsim]$_3$[PMo$_{12}$O$_{40}$]



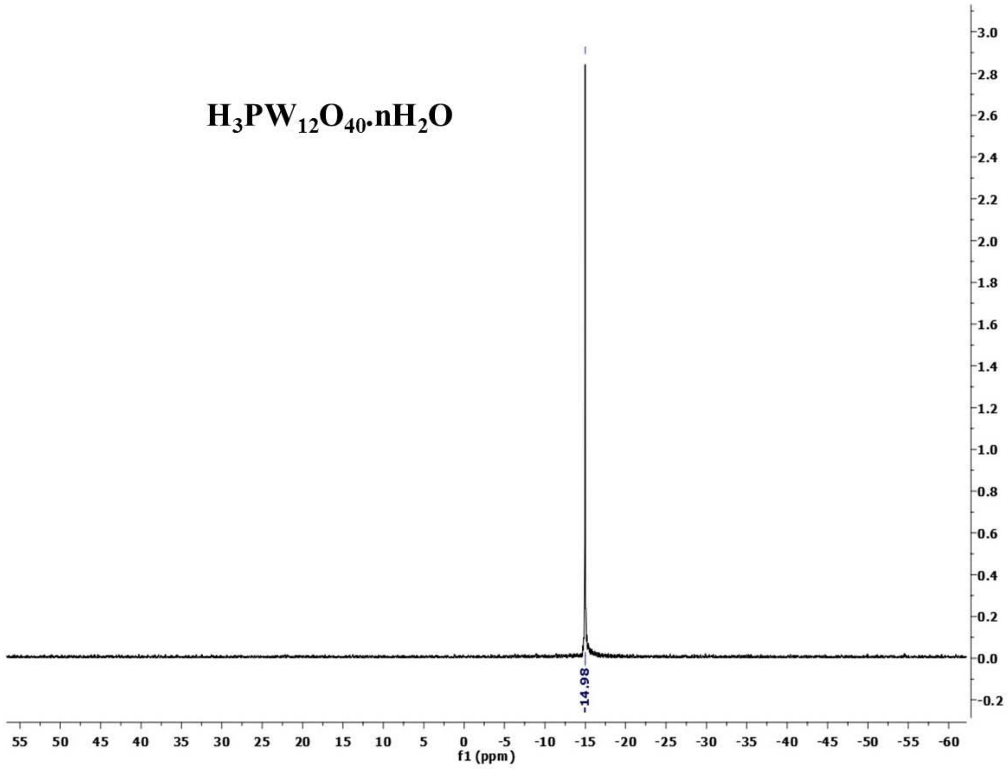
(a)

(b)

Fig.5B.2: ^{13}C NMR of (a) [mdsim]$_3$[PW$_{12}$O$_{40}$] & (b) [mdsim]$_3$[PMo$_{12}$O$_{40}$]

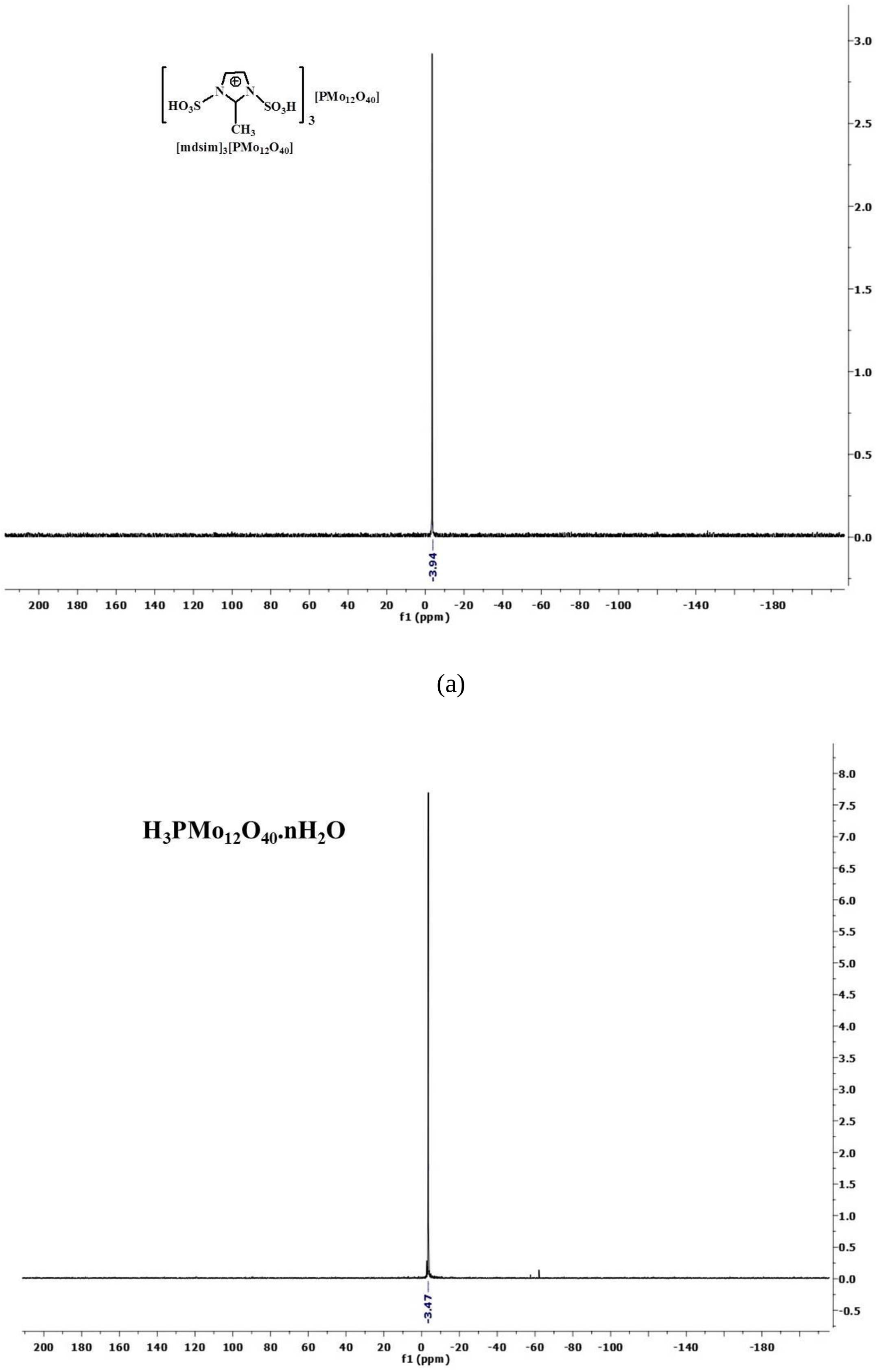


(a)



(b)

Fig.5B.3a: ^{31}P NMR spectra of (a) $[mdsim]_3[PW_{12}O_{40}]$ & (b) phosphotungstic acid



(a)

(b)

Fig.5B.3b: ^{31}P NMR spectra of (a) $[mdsim]_3[PMo_{12}O_{40}]$ & (b) phosphomolybdic acid

FT-IR analysis

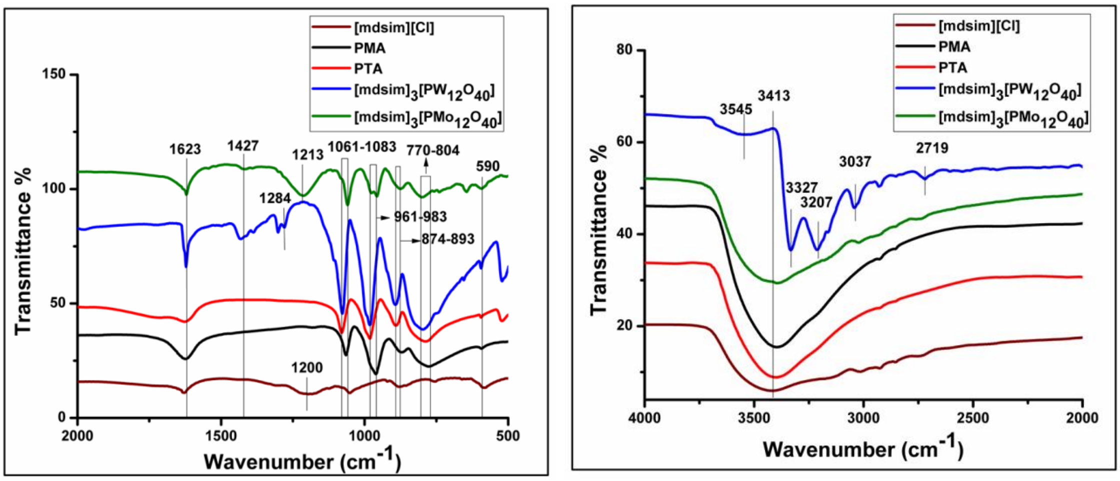


Fig.5B.4: FTIR spectra of $[mdsim]_3[PW_{12}O_{40}]$, $[mdsim]_3[PMo_{12}O_{40}]$, PTA, PMA and [mdsim][Cl]

To verify the presence of Keggin structure of heteropolyanions within the POM compounds, their FT-IR spectra were analyzed and compared in two regions within 500-200 cm^{-1} and 2000-4000 cm^{-1} in **Fig.5B.4**. The Keggin units $[PM_{12}O_{40}]^{3-}$ where M = W and Mo of the two salts expressed typical absorptions at 1061-1083 cm^{-1} (asymmetric P-O stretch), 961-983 cm^{-1} (asymmetric $M{=}O_t$ stretch), 874-893 cm^{-1} (asymmetric stretch of $M–O_{2c2}–M$ bonds of corner-sharing MO_6 octahedra), 770-804 $cm^{–1}$ (asymmetric stretch of $M–O_{2c1}–M$ bonds involving edge-sharing MO_6 octahedra) and 586-590 $cm^{–1}$ (P–O bending). The peak at 1623 cm^{-1} with medium intensity can be assigned for overlapped O-H bending with C=C stretching of imidazole ring. In addition, the small shoulder at 1427-1435 cm^{-1} can be expected for the imidazole ring vibration. The peak at 1213-1284 cm^{-1} could be attributed to S-O symmetric stretch of the $-SO_3H$ group. The S-O antisymmetric stretch may be observed in the same region of P-O stretch at 1061-1083 cm^{-1}. It is expected that vibration frequency of N-S stretch will exist within the absorption peak of Keggin anions at 874-893 cm^{-1}. The aliphatic C-H stretch of -Me group is distinctly observed at 2719, 2919, 3037 cm^{-1} for the hybrid salt of phosphotungstic acid. It also shows two strong absorptions at 3327 cm^{-1} and 3207 cm^{-1} which can be assigned for overlapped C-H stretch of imidazolium cation and O-H stretch of $-SO_3H$ groups involving strong intra molecular H-bonds with the phosphotungstate anion [97-99]. The weak O-H stretch of phosphotungstate hybrid compound at 3545cm^{-1} can be observed for very small amount of H-bonded water molecules around the Keggin anion after elimination of most of its water content through the dynamic dehydration equilibrium in strong Brönsted acidic environment of the material (**Equation 5B.1**). The medium strength broad shoulder of phosphomolybdate hybrid compound near 3413 cm^{-1} can be expected as a merged absorption of imidazolium C-H stretch, intra molecular H-bonded O-H stretch of -SO_3H groups in addition to minimum amount of strongly H-bonded water molecules in the rigid framework of Keggin $[PMo_{12}O_{40}]^{3-}$ anion. Thermogravimetric analyses also evidenced (**Fig.5B.5**) absence of loosely bound physisorbed water in the structures of hybrid POM salts and thus support the hydrophobic nature of the hybrid material.

TGA analysis

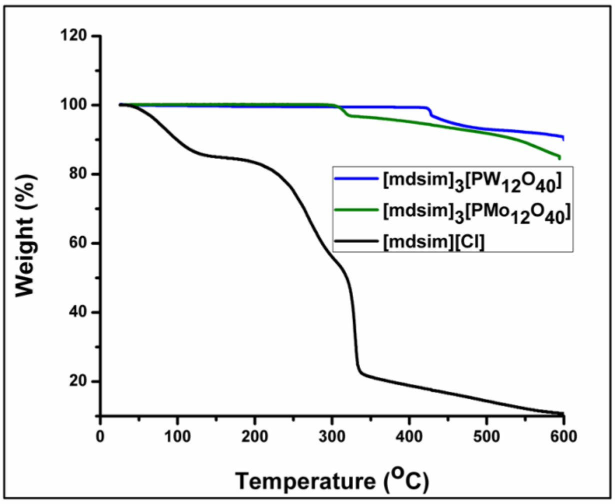


Fig.5B.5: TGA graph of POMs with respect to the parent [mdsim][Cl]

Thermogravimetric profile of the two POM salts simply specify their hydrophobic nature and severe increase in high thermal stability as compared to the parent ionic liquid [mdsim][Cl] (**Fig.5B.5**). Thermal stability of the $[mdsim]_3[PW_{12}O_{40}]$ salt is extended up to 440°C which is observed at 320°C for the $[mdsim]_3[PMo_{12}O_{40}]$ salt [100]. The initial 15% weight loss of parent IL around 100°C can be observed for physisorbed water followed by another slow decomposition in between 220°C to 320°C due to stepwise removal of the two -SO_3H groups and imidazole moiety.

PXRD analysis

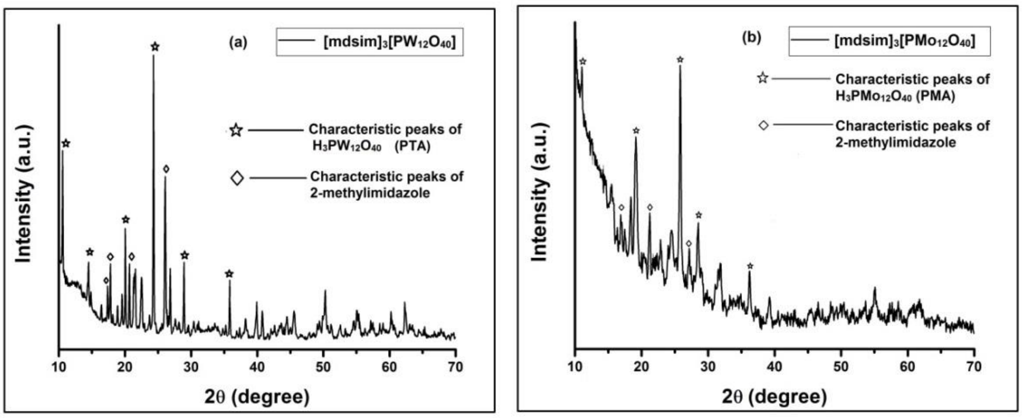


Fig.5B.6: Powder XRD analysis of two polyoxometalate salts

The Keggin structures of $[PW_{12}O_{40}]^{3-}$ and $[PMo_{12}O_{40}]^{3-}$ anions are retained in both 1, 3-disulfo-2-methyl-imidazolium POM salts as assessed from their characteristic powder XRD peaks (**Fig.5B.6**). In [mdsim]$_3$[PW$_{12}$O$_{40}$], strong reflections at 2θ = 10.6, 14.4, 20.1, 24.5, 29.0, 35.8 can be correlated with matched reflection planes (1 1 0), (2 0 0), (2 2 0), (2 2 2), (4 0 0), (3 3 2) of PXRD data base (JCPDS card number 75-2125, $H_3PW_{12}O_{40}$). Similarly, the intense peaks of [mdsim]$_3$[PMo$_{12}$O$_{40}$] with 2θ = 11.0, 19.2, 25.9, 28.6, 36.1 can be considered for the reflection planes (1 1 0), (2 1 2), (0 0 6), (3 0 5), (4 2 2) of JCPDS card number 46-0482 ($H_3PMo_{12}O_{40}$). Both the JCPDS card numbers indicate that the Keggin structures of the corresponding acids are preserved in the POM salts. Other sharp peaks at 2θ = 17.4, 17.9, 21.5, 26.05 can be accounted for 2-methylimidazolium unit [101, 102].

Raman analysis

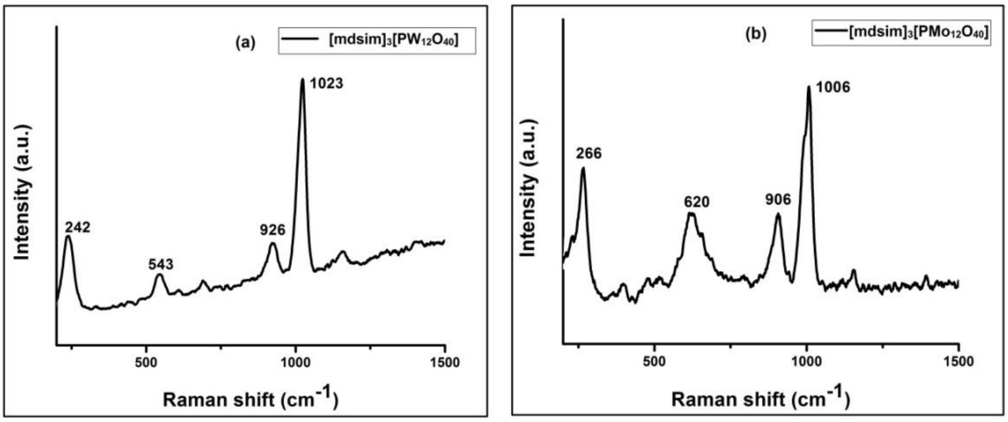
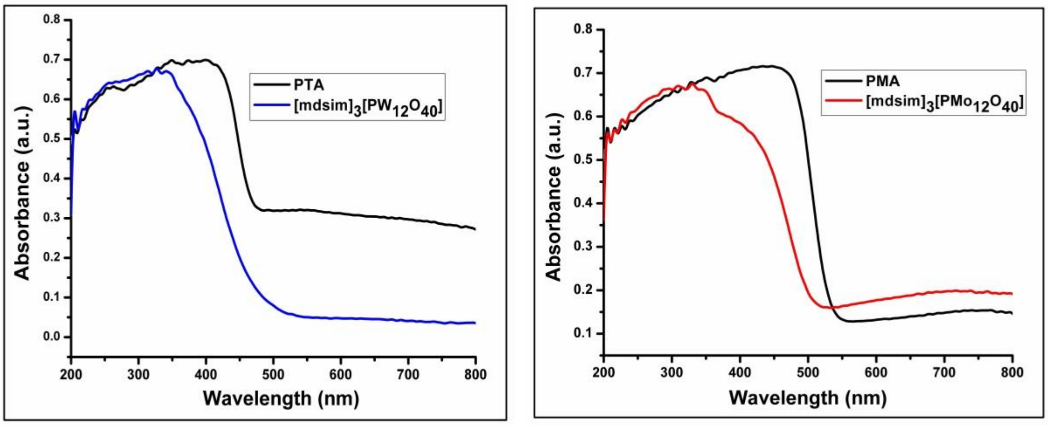


Fig.5B.7: Raman spectra of the polyoxometalates

Raman spectra for the POM salts are displayed in **Fig.5B.7**. The presence of Keggin structured heteropolyanions $[PW_{12}O_{40}]^{3-}$ and $[PMo_{12}O_{40}]^{3-}$ were evidenced from typical Raman bands as observed according to Bridgeman's assignments [103, 104]. In $[mdsim]_3[PW_{12}O_{40}]$, the sharp intense peak at 1023 cm^{-1} is observed for symmetric stretching mode of W-O_t bond along with another weak band at 926 cm^{-1} for asymmetric W-O_{2c2}-W stretch. The weak band at 543 cm^{-1} is attributed to combined stretching and bending vibrations of W-O_{2c1}-W, W-O_{2c2}-W and O-P-O bonds. Furthermore, the medium intensity peak at 242 cm^{-1} can be expected from W-O_{4c} stretch and W-O_{2c2}-W bending vibrations.

Similarly, in case of the $[mdsim]_3[PMo_{12}O_{40}]$ salt, the strong band at 1006 cm^{-1} can be assigned to symmetric stretch of terminal Mo-O_t bond followed by another shoulder at 979 cm^{-1} corresponding to asymmetric stretch of the same bond. The medium strength "inter ligand vibration" defined by Bridgeman at 906 cm^{-1} is observed for asymmetric Mo-O_{2c2}-Mo stretch [104]. Another broad peak at 620 cm^{-1} may be resulted from combined stretching and bending vibration of Mo-O_{2c1}-Mo bonds of the Mo_3O_{13} groups. The sharp band at 266 cm^{-1} can be accounted for stretching vibration of Mo-O_{4c} bonds and bending of the intraligand Mo-O_{2c2}-Mo bonds [104].

UV-Vis diffuse reflectance spectra



(a) (b)

Fig.5B.8: UV-Vis diffuse reflectance spectra of (a) $[mdsim]_3[PW_{12}O_{40}]$ with $H_3PW_{12}O_{40}$ (PTA) and (b) $[mdsim]_3[PMo_{12}O_{40}]$ with $H_3PMo_{12}O_{40}$ (PMA)

The existence of Keggin structure of $[PM_{12}O_{40}]^{3-}$ where M = W and Mo can be evidenced from their identical UV-DRS absorption with the corresponding heteropolyacids (HPAs) (**Fig 5B.8**).

SEM analysis

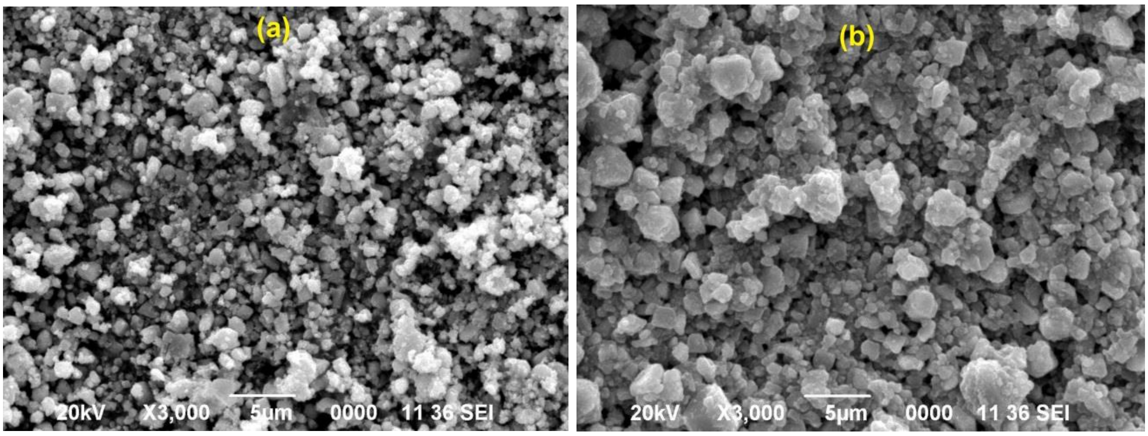


Fig.5B.9: SEM images of (a) $[mdsim]_3[PW_{12}O_{40}]$ & (b) $[mdsim]_3[PMo_{12}O_{40}]$

The surface morphology of $[mdsim]_3[PW_{12}O_{40}]$ indicates heterogeneous surface with smaller size crystalline particles and clusters in **Fig.5B.9(a)**. The crystallinity of $[mdsim]_3[PMo_{12}O_{40}]$ particles is higher as compared to the phosphotungstate POM salt in **Fig.5B.9(b)**. The sizes of crystalline particles are bigger with minimum clustering on its surface. The agglomeration of each solid material can be expected as an outcome of secondary interactions *via* intermolecular H-bonds of $-SO_3H$ functionality of imidazolium cation.

EDX analysis

Fig.5B.10 expressed the presence of key elements of the POM salts in their respective energy dispersive X-ray (EDX) images except the detection of P atom in the spectrum of $[mdsim]_3[PW_{12}O_{40}]$ salt. Disappearance of the P atom can be assumed as low abundance of this element within the complex and large cage of Keggin anion as compared to oxygen (O) and tungsten atoms (W). However, the ^{31}P NMR spectrum of this salt confirmed the presence of P atom in the Keggin structured anion (**Fig.5B.3a**). The energy dispersive X-ray mapping of hybrid materials revealed uniform dispersion of the component elements for the two salts in **Fig.5B.11(a)** and **Fig.5B.11(b)**.

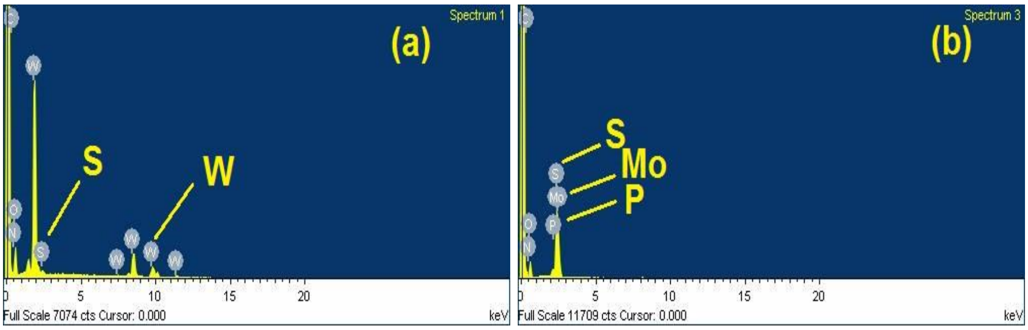


Fig.5B.10: EDX images of (a) $[mdsim]_3[PW_{12}O_{40}]$ and (b) $[mdsim]_3[PMo_{12}O_{40}]$

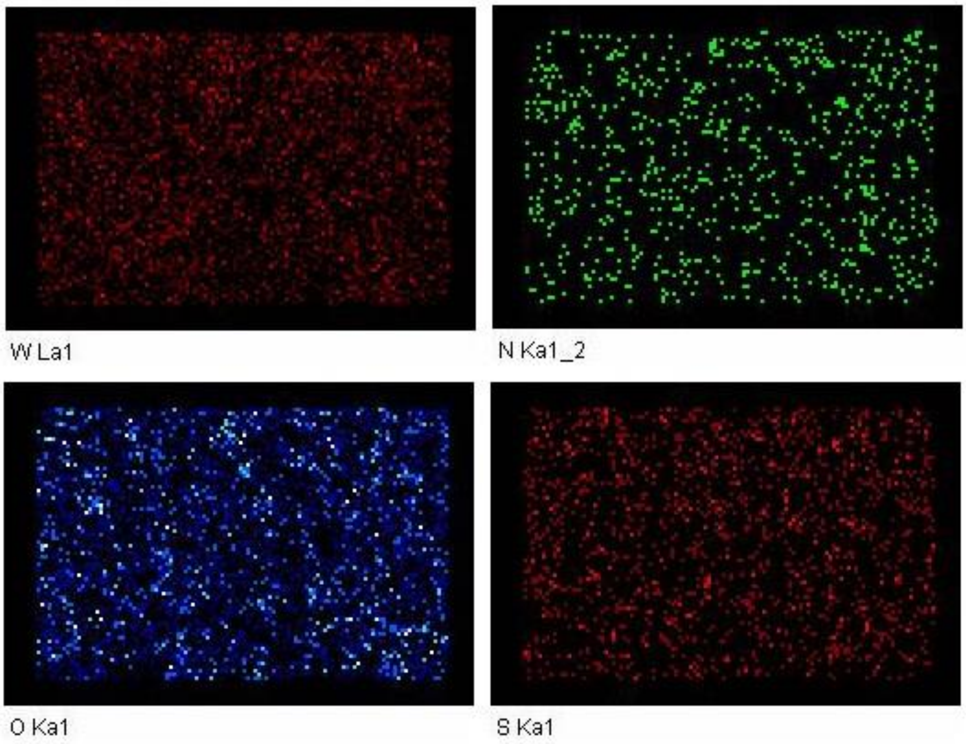


Fig.5B.11(a): EDX mapping of N, S, O and W for $[mdsim]_3[PW_{12}O_{40}]$

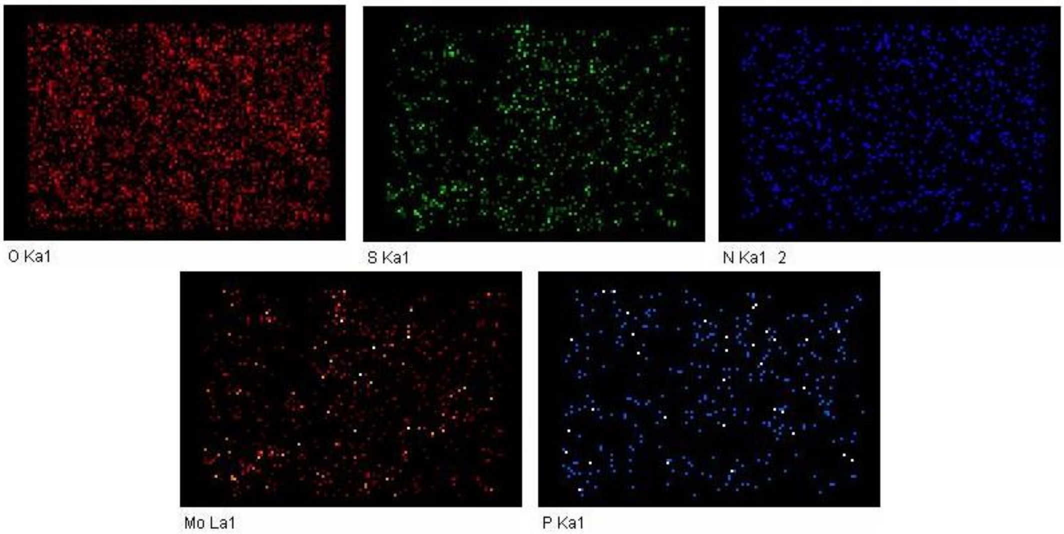


Fig.5B.11(b): EDX mapping of N, S, O, P and Mo for $[mdsim]_3[PMo_{12}O_{40}]$

Hammett acidity determination by UV-Visible

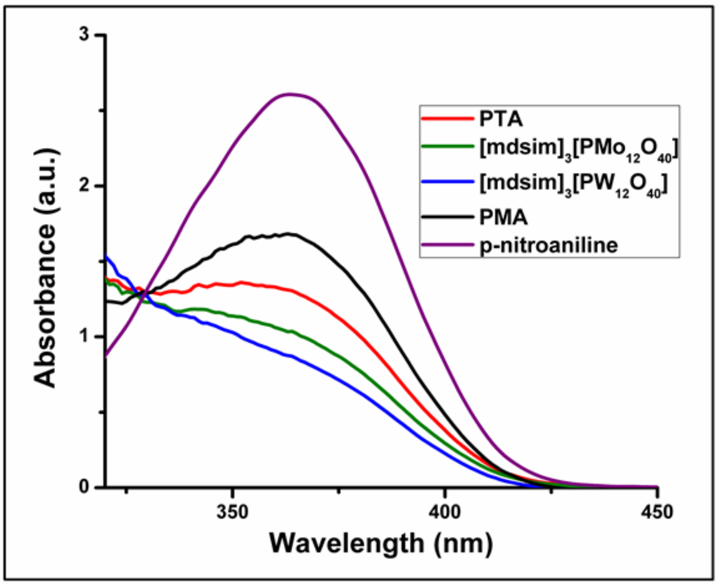


Fig.5B.12: Hammett plots of 2-methyl disulfoimidazolium POM salts with respect to the parent acids

Determination of Brönsted acidity of the POM salts by Hammett acidity method utilized 4-nitroaniline as spectrophotometric basic indicator and CH_3CN as polar aprotic solvent according to standard procedure described in earlier section (**Section 2B**) [105]. Characteristic absorbance of the basic indicator decreases with increased acidity of the acidic POM ionic salts as the degree of protonation enhanced with their acidic strength

(**Fig.5B.12**). The acidity order was found as $[mdsim]_3[PW_{12}O_{40}]$ > $[mdsim]_3[PMo_{12}O_{40}]$ > PTA > PMA from the calculated Hammett acidity function in **Table 5B.1**.

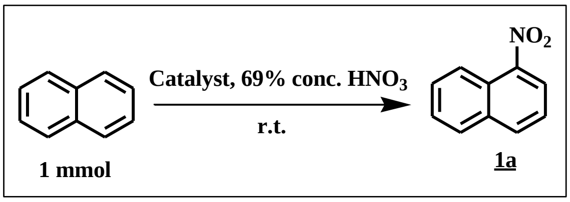
Table 5B.1: Calculation of Hammett acidity function (H^o)

Entry	A_{max}	[I] %	$[IH^+]$ %	H^o
p-niroaniline	2.60	100	0	-
PMA	1.50	57.6	42.4	1.02
PTA	1.29	49.6	50.4	0.98
$[mdsim]_3[PMo_{12}O_{40}]$	1.02	39.2	60.8	0.79
$[mdsim]_3[PW_{12}O_{40}]$	0.86	33.2	66.8	0.68

5B.2 Catalytic activity

Catalytic activity of the hybrid compounds was investigated for nitration of various aromatic hydrocarbons containing electron withdrawing or donating groups in the benzene ring. The varied catalysts amount of $[mdsim]_3[PW_{12}O_{40}]$ such as 0.16, 0.32 and 0.64 mol% were initially studied for optimization reaction of naphthalene (1 mmol) with 69% HNO_3 (3 mmol) at room temperature stirring in **Table 5B.2** (entry 1) in absence of any additional solvent. The reaction showed best catalytic activity using 0.32 mol% the catalyst by taking 5 min time to produce 98% yield of the product (**Table 5B.2**, entry 1). This optimized amount of catalyst was also used for conducting the same reaction with the other catalyst $[mdsim]_3[PMo_{12}O_{40}]$ under identical condition with a lower catalytic activity (**Table 5B.2**, entry 2). Then it was decided to increase the amount to 0.5 and 1 mol% of this catalyst to get better outcomes (**Table 5B.2**, entry 2) which was found for 0.5 mol% of the catalyst. Also varying the reactant and HNO_3 (69%) ratio to 1:1 and 1:2 gave different results (**Table 5B.2**, entries 3 & 4) which concluded that 1:3 ratio of substrate and HNO_3 brought satisfactory result in case of the optimization reaction in presence of 0.32 mol% of the $[mdsim]_3[PW_{12}O_{40}]$ salt (**Table 5B.2**, entry 1) and 0.50 mol% of the $[mdsim]_3[PMo_{12}O_{40}]$ salt (**Table 5B.2**, entry 2). **Table 5B.3** displayed comparison of catalytic activity of $[mdsim]_3[PW_{12}O_{40}]$ with other reported catalysts for nitration of toluene. The substrate scope study was extended with these optimized amounts of catalysts for electron rich and electron deficient aromatic compounds with varied amount of 69% HNO_3 as nitrating agent as included in **Table 5B.4**. It was observed that electron deficient system required 80°C and more acid to undergo nitration (**Table 5B.4**, entries 3, 4, 6) whereas hydrocarbons and phenolic compounds (**Table 5B.4**, entries 1, 2, 5, 7, 8) easily nitrated at room temperature in presence of minimal nitric acid. Nitration of phenol was not possible with these catalysts because of oxidative degradation. Aniline also didn't form any nitration product and leaded to formation of some complex mixture of polar products involving -SO_3H functionalized acidic hybrid material. Acetanilide also displayed the progress of reaction followed by hydrolysis of amide bonds in strong acidic solution. Aromatic aldehydes without electron donating groups were inactive for the nitration reaction and produced oxidative side products. Interestingly, nitration of 4-hydroxy benzaldehyde yielded 4-hydroxy-3-nitrobenzaldehyde at 80°C with excess amount of nitric acid within short time without oxidation of aldehyde group (**Table 5B.4**, entry 6).

Table 5B.2: Optimization of POMs catalyst amount for nitration of naphthalene



Entry	Catalyst	Amount (mol%)	Time (min)	Yield (%) **1a**
1	$[mdsim]_3[PW_{12}O_{40}]^a$	0.16/**0.32**/0.64	15/**5**/5	92/**98**/98
2	$[mdsim]_3[PMo_{12}O_{40}]^a$	0.32/**0.50**/1	20/**10**/10	90/**96**/98
3	$[mdsim]_3[PW_{12}O_{40}]/[mdsim]_3[PMo_{12}O_{40}]^b$	0.30/0.50	20/30	25/20
4	$[mdsim]_3[PW_{12}O_{40}]_3/[mdsim]_3[PMo_{12}O_{40}]^c$	-do-	20/25	68/65

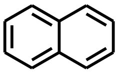
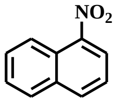
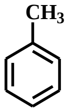
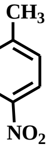
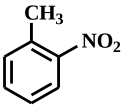
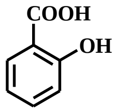
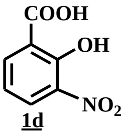
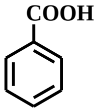
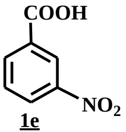
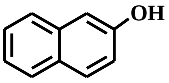
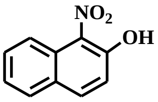
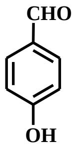
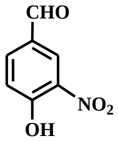
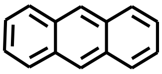
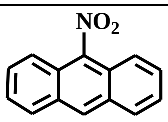
[a] Nitration was carried out using 1:3 ratio of naphthalene and 69% HNO_3 acid at room temperature; [b] using 1:1 ratio of naphthalene & 69% HNO_3; [c] using 1:2 ratio of naphthalene & 69% HNO_3 with best mol% of the two catalysts.

Table 5B.3: Comparison of catalytic activity for nitration of toluene

Entry	Catalyst	Temp (°C)	Time (h)	Yield (%)
1	$[mdsim]_3[PW_{12}O_{40}]$	r.t.	0.25	94
2	$Yb(OSO_2C_8F_{17})_3/C_{10}F_{18}/95\%\ HNO_3$	60	48	70 [71]

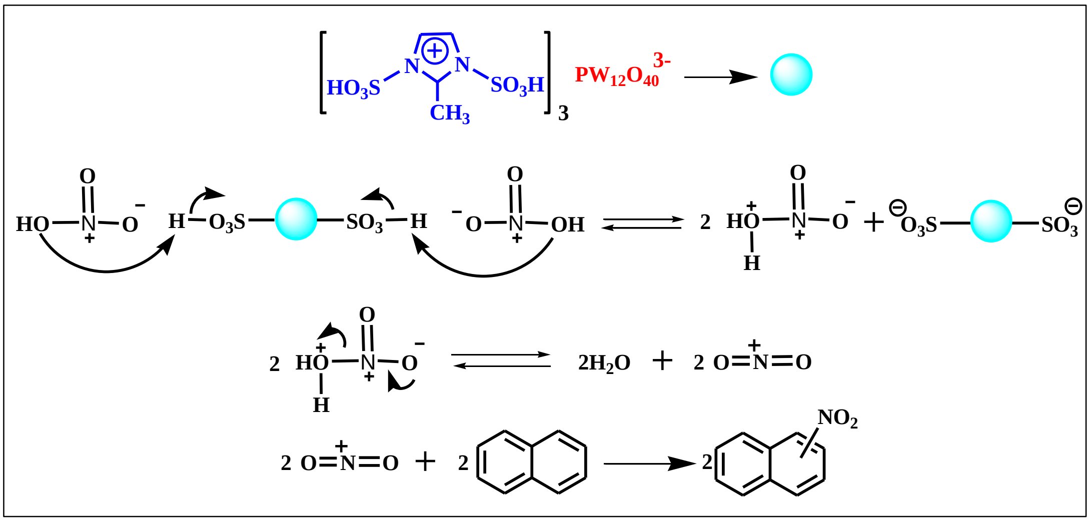
3	HNO_3-Ac_2O/CH_2Cl_2/[bmpy][NTf_2]	25	1	70 [79]
4	$Bi(NO_3)_3.5H_2O$/[bmim][PF_6]	85	1.5	100 [86]

Table 5B.4: Substrate scope study for nitration of aromatic compounds using hybrid catalysts

Entry	Substrates	Products	Time (min)^a A/B	Temp (°C)	Yield (%)$^{b, f}$ A/B
1		 **1a**	5/10^c	r.t.	98/96
2		 **1b**  **1c**	15/20^c	r.t.	64:30 (A)^e 62:27 (B)
3		 **1d**	15/20^d	80^{o}C	95/92
4		 **1e**	10/12^d	80^{o}C	90/88
5		 **1f**	10/15^c	r.t.	90/90
6		 **1g**	20/28^d	80^{o}C	85/80
7		 **1h**	10/15^c	r.t.	90/85

[a] A & B were used to represent [mdsim]$_3$[$PW_{12}O_{40}$] and [mdsim]$_3$[$PMo_{12}O_{40}$] catalysts; [b] Isolated yields; [c] Reactant: conc.HNO_3 = 1:3; [d] Reactant: conc.HNO_3 = 1:10; [e] Selectivity of *p*- and *o*-products are calculated based on isolated yields of products; [f] All the nitro compounds were known compounds and also characterized by their melting points, ^{1}H NMR, ^{13}C NMR and IR analysis.

Plausible reaction mechanism



Scheme 5B.1: Mechanism for nitration of naphthalene using POM salt as catalyst

The proposed mechanism followed the usual path for formation of nitronium ion from the interaction of –SO_3H group of the catalyst with nitric acid which later acts as electrophile to give nitro product.

Recyclability study

The catalytic recyclability was studied for 5 mmol of naphthalene with 15 mmol of 69% HNO_3 at room temperature stirring with optimized amount of catalyst $[mdsim]_3[PW_{12}O_{40}]$ for the specified reaction time (**Table 5B.3**, entry-1). The catalyst was recovered as solid residue from acidic solution of water after completion of the reaction by following the standard work-up steps as described in general method of nitration reaction (**Experimental section**, subunit **5B.4**). **Fig.5B.13** expressed the reusability profile of spent catalyst with descending order of catalytic activity for four consecutive runs that may be expected for loss of small amount of the used catalyst during repeated isolation in every cycle. After 4th cycle of the reaction, the reused catalyst almost retains the original pattern of PXRD and FT-IR spectrum (**Fig.5B.14**) similar to the fresh POM salt.

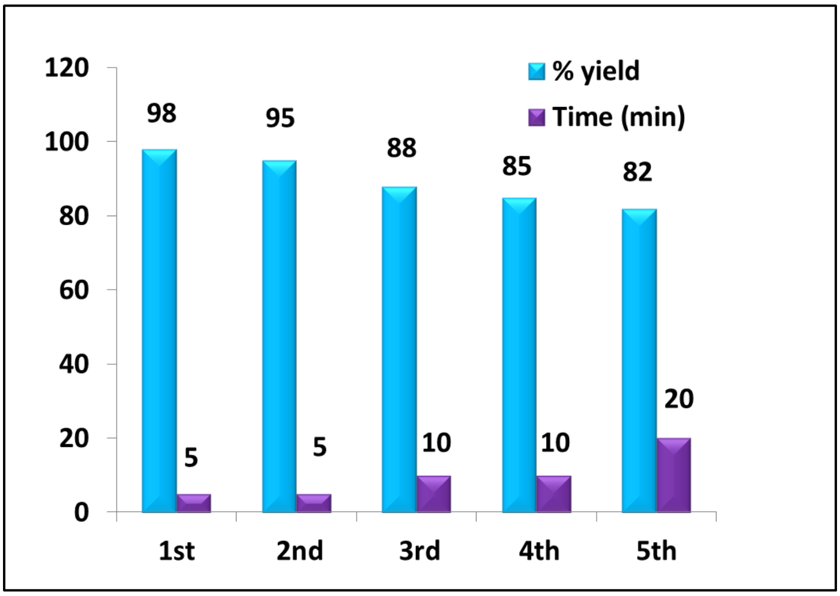
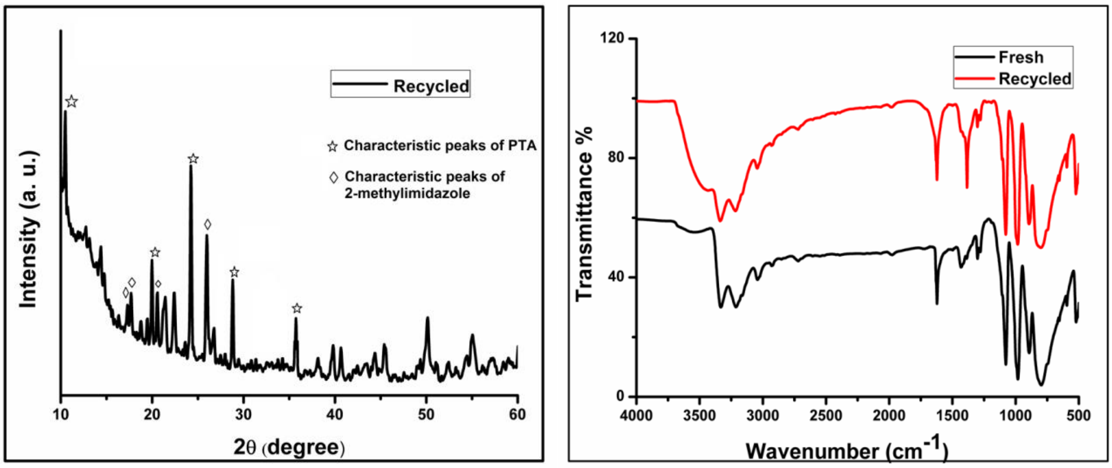


Fig.5B.13: Reusability profile of the $[mdsim]_3[PW_{12}O_{40}]$ catalyst



(a) (b)

Fig.5B.14: (a) PXRD and (b) FT-IR spectra of fresh and recycled $[mdsim]_3[PW_{12}O_{40}]$ catalyst

5B.3 Conclusion

In conclusion, this work developed two thermal and water stable hydrophobic -SO_3H functionalized imidazolium based polyoxometalate hybrid salts of corresponding heteropolyacids namely phosphotungstic and phosphomolybdic acid as solid acidic materials. The internal -SO_3H groups of these salts function as equivalent of concentrated sulfuric acid reagent during nitration of aromatic compounds in combination with stoichiometric amount of 69% HNO_3 at room temperature and 80°C depending on the nature of electron rich and electron deficient aromatic substrates. Thus, catalytic use of these hydrophobic POM salts introduced several advantages to the aromatic nitration as compared to traditional nitration involving excess amount of concentrated H_2SO_4 and HNO_3 mixture. These include complete replacement of corrosive sulfuric acid, controlled use of 69% nitric acid, mild reaction procedure, minimal reddish brown vapor of nitrogen dioxide, simple isolation of product, recycling of catalyst in heterogeneous phases, shorter reaction time and also release of less acid waste. These studies showed slight differences of catalytic activity of the two salts which was observed to be higher for the $[mdsim]_3[PW_{12}O_{40}]$ against its minimum value of Hammett acidity function. The acidity of the catalyst coming from -SO_3H functionality along with structural stability originated from POM anion are two factors enhancing the nitration reaction in a mild way. Thus, this method offers a simple and safer route to synthesize nitro compounds without using hazardous acids.

5B.4 Experimental section

General techniques

The required chemicals were purchased from TCI Chemicals. Description of analytical instruments used for characterization of the POM hybrids and aromatic nitro compounds were identical with the "**General Information**" of **Chapter 2**, **Section 2B** under experimental section.

Preparation of 2-methyl-1, 3-disulfoimidazolium salts of Keggin anions $[mdsim]_3[PM_{12}O_{40}]$ where M= W and Mo

The preparation of hybrid of 2-methyl-1, 3-disulfoimidazolium heteropolyanions of Keggin units $[PM_{12}O_{40}]^{3-}$ where M = W & Mo were completed in two step process (**Scheme 5A.16**, **Section 5A**). The parent ionic liquid 2-mehyl-1, 3-disulfoimidazolium chloride [mdsim][Cl] was prepared through drop wise addition of chlorosulfonic acid (20 mmol) to a stirred solution of 2-methyl imidazole (10 mmol) in dry CH_2Cl_2 (30 mL) in a 100 mL round bottom flask at 0°C for 10 min under nitrogen atmosphere. Then the mixture was stirred at room temperature for one hour to complete the reaction. The brown viscous ionic liquid formed a separate layer with dichloromethane which was later removed through decantation process. Repeated addition and decantation of dry CH_2Cl_2 (3×10 mL) were done for three more times for purification of the ionic liquid phase by dissolving dichloromethane soluble impurities. Drying the residue in vacuum oven at 50°C yielded 95% of the product as brown viscous liquid.

The 2nd step was done by treatment of phosphotungstic acid hydrate ($H_3PW_{12}O_{40}.nH_2O$) or phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}.nH_2O$) with the parent [mdsim][Cl] ionic liquid in 1:3 ratio to achieve the desired heteropolyoxometalate salts $[mdsim]_3PM_{12}O_{40}$ (where M = W & Mo) as strong acidic solid materials (**Scheme 5A.16**). To a stirred aqueous solution (20 mL of water) of the respective heteropolyacid (2 mmol), viscous ionic liquid (6 mmol) was added drop wise at room temperature within 5 min. Formation of white and yellow precipitates was observed for the $[mdsim]_3[PW_{12}O_{40}]$ and $[mdsim]_3[PMo_{12}O_{40}]$ compounds respectively after 12 hour stirring at room temperature. Then the precipitate was centrifuged and washed with distilled water for 3-4 times. The pure heteropolyoxometalate salts were dried in vacuum oven at 80^{o}C for overnight to get 98-99% yields of the products.

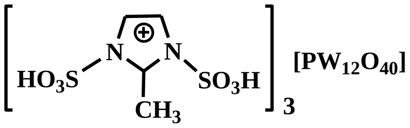
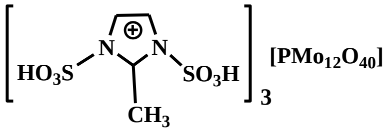
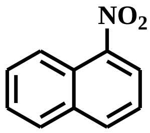
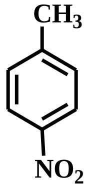
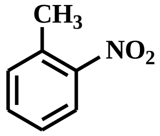
Typical procedure for nitration of aromatic compounds

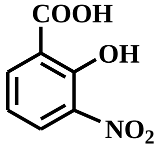
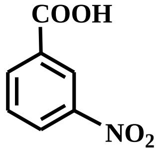
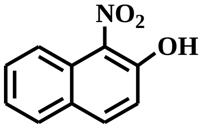
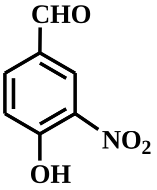
Nitration of various aromatic compounds was done by direct treatment of aromatic substrate (1 mmol) with 69% concentrated HNO_3 (0.12 mL, 3 mmol) in presence of 0.3 mol% of $[mdsim]_3[PW_{12}O_{40}]$ or 0.5 mol% of $[mdsim]_3[PMo_{12}O_{40}]$ catalysts in a 50 ml round bottom flask fitted with an air condenser at room temperature stirring or different temperature to get desired nitro aromatic compounds (**Scheme 5B.1**). Ice cold (5 mL) water was added to stop the reaction upon completion (monitored by TLC) and the nitro product was extracted with dichloromethane (3x5 mL) from the aqueous solution of reaction mixture. The organic extract was dried over anhydrous sodium sulfate and evaporated to get solid (or liquid) crude nitro products. The catalyst dispersed in aqueous extract was recovered as solid residue after evaporation of water under reduced pressure and then dried in vacuum oven at 80^{o}C for reactivation of the catalyst. Further purification of the nitro products were done using preparative TLC technique or recrystallization from suitable solvent based on the single product selectivity or physical state of crude nitro products.

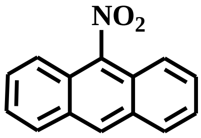
Procedure for Hammett acidity calculation

The Hammett acidity determination method is already discussed in the experimental section of **Chapter 2B**.

5B.5 Spectral data

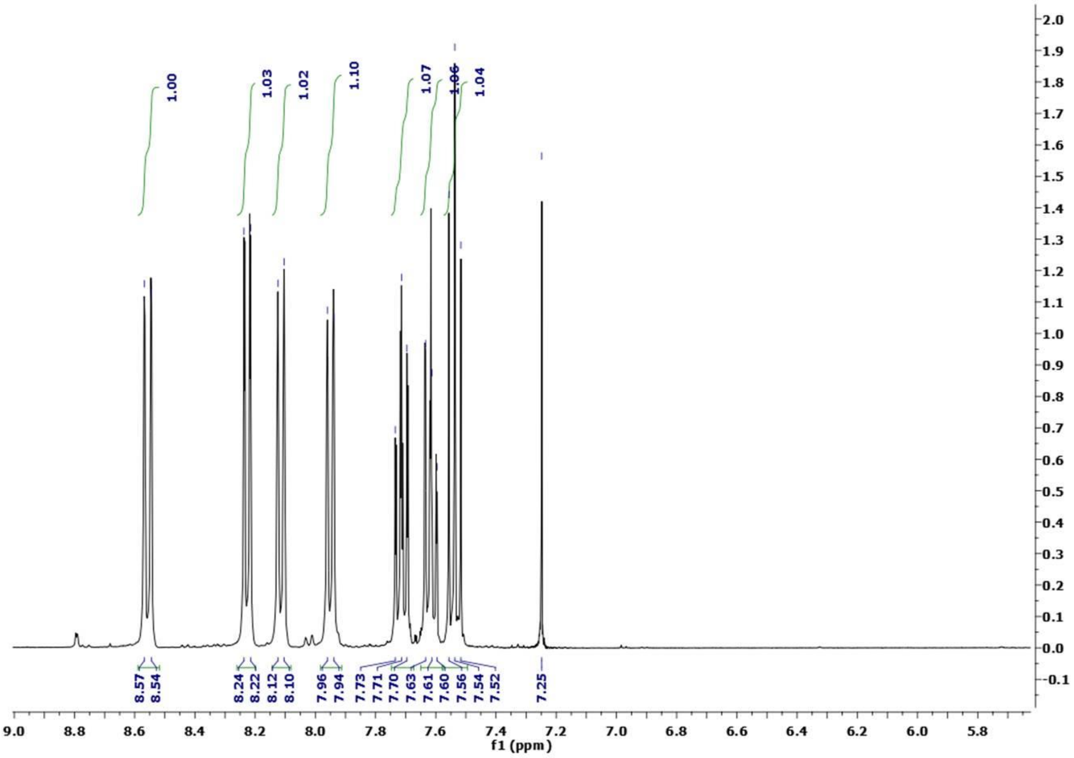
Entry	Spectral data
 **[mdsim]$_3$[PW$_{12}$O$_{40}$]**	White solid; FT-IR (KBr) cm^{-1}: 3331, 3213, 3042, 2927, 1623, 1247, 1284, 1061, 1083, 961, 874; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 13.77 (s, 2H), 7.49 (m, 2H), 2.51 (s, 3H);^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 144.6, 119.0, 11.5; ^{31}P NMR: (DMSO-d$_6$, 202 MHz): δ-15.25.
 **[mdsim]$_3$[PMo$_{12}$O$_{40}$]**	Yellow solid; FT-IR (KBr) cm^{-1}: 3390 (brs), 1623, 1213, 1061, 1083, 961, 778, 596; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 13.78 (s, 2H), 7.49 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 144.6, 119.0, 11.5; ^{31}P NMR: (DMSO-d$_6$, 202 MHz): δ -3.94.
Spectra of nitro compounds	
 **1-nitronaphthalene** **1a**	Light yellow solid, Mp.: 59-61°C; FT-IR (KBr) cm^{-1}: 3435, 2852, 1568, 1520, 1357, 1337, 1259, 1028, 871, 804, 789, 761, 500; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.57 (d, J = 12 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 8.0Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.7, 134.4, 129.5, 128.7, 127.4, 125.1, 124.2, 124.1, 123.2.
 **1-methyl-4-nitrobenzene** **1b**	Pale yellow solid, Mp.: 51-52°C; FT-IR (KBr) cm^{-1}; 3449, 3086, 2930, 2849, 1921, 1595, 1513, 1343, 1179, 1105, 1039, 860, 786, 728, 668, 601, 527; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, J = 12.0 Hz, 2H), 7.31 (d, J = 12.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 146.0, 130.0, 124.6, 123.2, 21.6.
 **1-methyl-2-nitrobenzene** **1c**	Brown liquid; FT-IR (KBr) cm^{-1}; 3441, 3082, 2930, 2847, 1921, 1596, 1511, 1340, 1175, 1101, 1037, 862, 786, 729, 665, 605, 522; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H),

	7.36-7.31 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.9, 135.2, 133.2, 129.8, 126.9, 120.8, 20.4.
 **2-hydroxy-3-nitrobenzoic acid** **1d**	Yellow solid, Mp.: 145-147°C; FT-IR (KBr) cm^{-1}: 3096, 2575, 1671, 1514, 1475, 1443, 1339, 1238, 1194, 1074, 856, 798, 572; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.97 (s, 1H), 8.27 (d, J = 12.0 Hz, 2H), 7.86-7.84 (m, 2H), 7.77-7.73 (m, 2H), 7.67-7.64 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 170.4, 148.9, 136.1, 130.5, 126.8, 119.1.
 **3-nitrobenzoic acid** **1e**	Pale yellow solid, Mp.: 139-140°C; FT-IR (KBr) cm^{-1}: 3096, 2575, 1671, 1514, 1475, 1443, 1339, 1238, 1194, 1074, 856, 798, 572; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.92-7.89 (m, 2H), 7.48-7.43 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 167.8, 148.4, 135.9, 133.1, 131.3, 129.8, 123.8.
 **1-nitronaphthalen-2-ol** **1f**	Reddish yellow solid, Mp.: 103-104°C; FT-IR (KBr) cm^{-1}: 3422, 3104, 3075, 2923, 2851, 1614, 1528, 1492, 1456, 1420, 1332, 1217, 1167, 1036, 971, 827, 725, 581; ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.07 (d, J = 8.0 Hz, 1H), 8.74 (s, 1H), 8.49 (dd, J = 12 Hz, 2.8 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 12 Hz, 1H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.5, 139.5, 130.2, 127.7, 124.9, 124.1, 122.2.
 **4-hydroxy-3-nitrobenzaldehyde** **1g**	Yellow solid, Mp.: 140-142°C; FT-IR (KBr) cm^{-1}: 3229, 2889, 1685, 1567, 1534, 1420, 1361, 1265, 1113, 960, 792, 742, 539; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.85 (s, 1H), 8.40 (s, 1H), 8.00 (d, J = 12.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 3.30 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 190.6, 157.5, 134.8, 128.8, 120.6, 100.1.

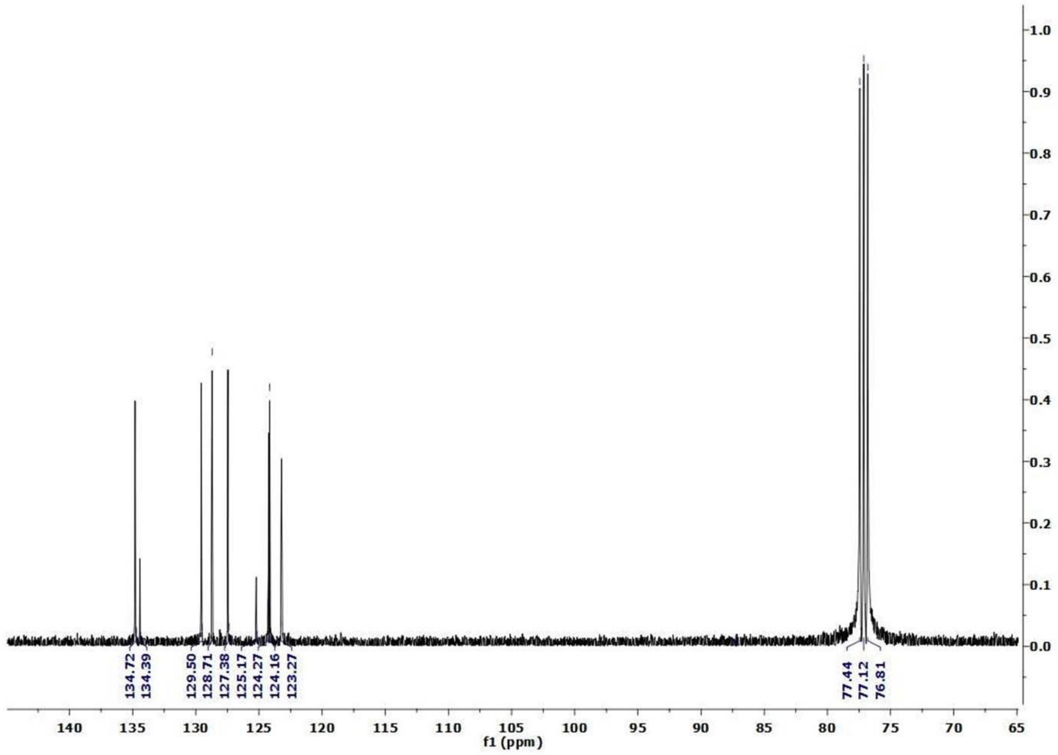
 **9-nitroanthracene** **1h**	Yellow solid, Mp.: 141-142^{o}C; FT-IR (KBr) cm^{-1}: 3436, 3058, 2922, 2852, 1676, 1516, 1454, 1371, 1442, 1371, 1318, 1275, 889, 773, 436; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.97 (s, 1H), 8.27 (d, J = 12.0 Hz, 2H), 7.86-7.84 (m, 2H), 7.77-7.73 (m, 2H), 7.67-7.64 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 146.1, 135.2, 131.4, 130.8, 130.3, 129.0, 126.9, 122.0, 120.6.

5B.6 NMR spectra of selected compounds

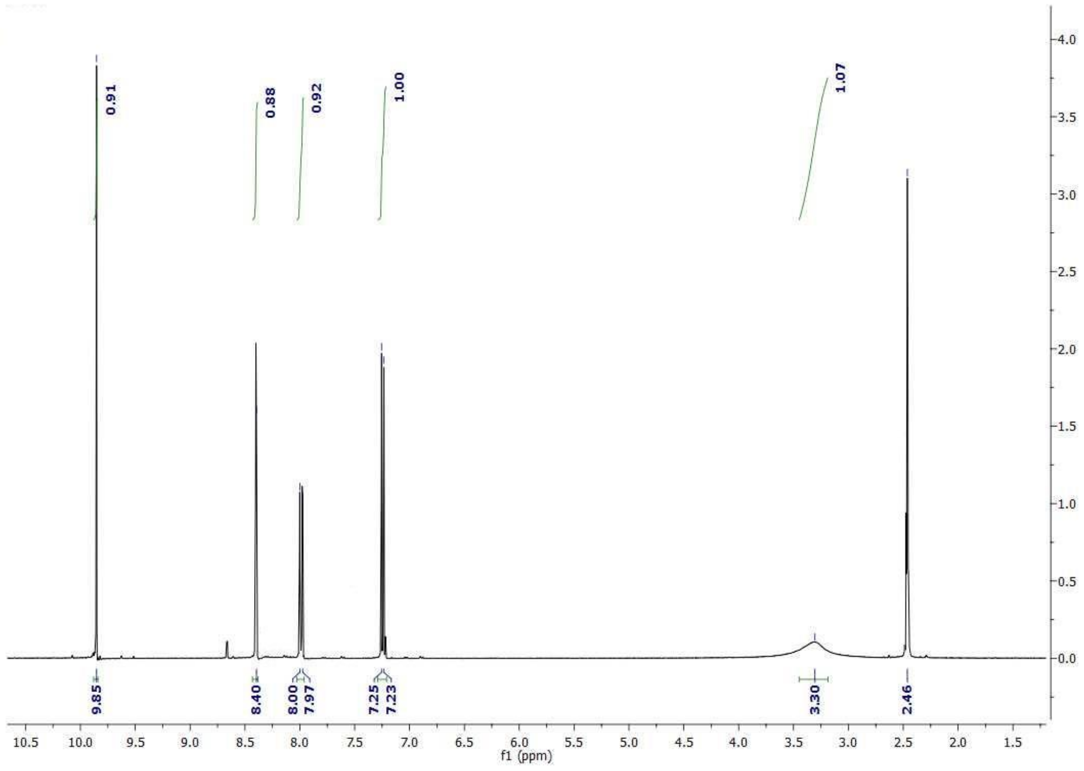
1. ^{1}H NMR of **1a**



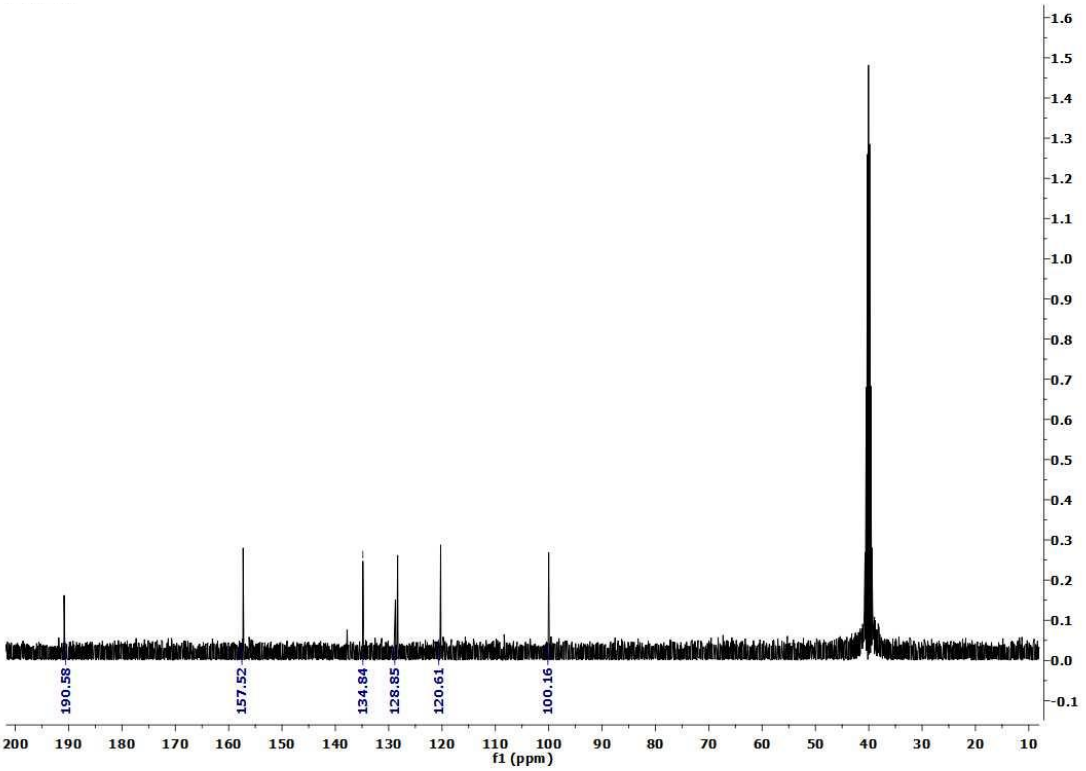
^{13}C NMR of **1a**



2. ^{1}H NMR of **1g**



^{13}C NMR of **1g**



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