

Investigation of hybrid molecular material prepared by ionic liquid and polyoxometalate anion[†]

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Abstract. A solid hybrid molecular material containing 1-butyl 3-methyl imidazolium cations and Keggin anions of phosphotungstic acid has been synthesized. It is fully characterized by CHN analysis, FTIR, XRD, UV-Vis-NIR DRS, ³¹P MAS NMR, TGA and SEM. The FTIR spectrum of the compound shows the fingerprint vibrational bands of both Keggin molecular anions and imidazolium cations. The aromatic C–H stretch region (2700–3250 cm⁻¹) of imidazolium cation is split due to the interaction between the ring C–H and bulky Keggin anion. The red-shift in the UV-Vis spectra and the downfield ³¹P MAS NMR chemical shift also confirm the electrostatic interaction between the ions in the compound. Near IR spectral region (1000–2500 nm) shows the elimination of water in the compound which is hydrophobic.

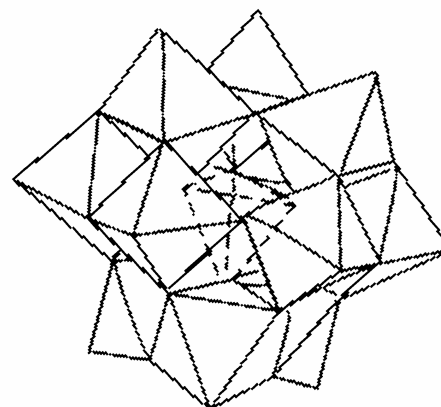
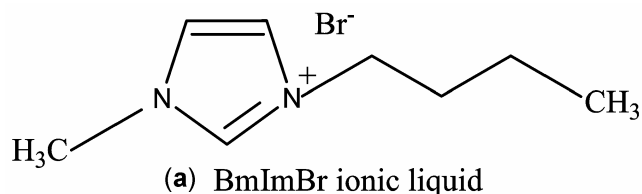
Keywords. 1-Butyl 3-methyl imidazolium bromide; molecular material; phosphotungstic acid; near IR.

1. Introduction

Ionic liquids are gaining importance in the synthesis of hybrid materials.¹ The ‘ionic liquid’ moniker is used for low melting point salts that contain organic cations.² Most of these organic salts are fluids below the boiling point of water, often even lower than the room temperature.³ They exhibit fascinating range of properties which include non-volatility, high thermal stability, non-flammability, good electrical conductivity and wider electrochemical properties.^{3,4} They have been extensively used in the synthesis of novel hybrid materials.^{1,5–10} The most common ionic liquids (IL) employed are imidazolium, pyridinium derivatives, phosphonium and tetralkylammonium compounds. The room temperature ionic liquidity is achieved by tailoring cations and anions to disturb salt’s normally highly crystalline nature. For example, the melting point of NaCl can be brought down from 803°C to 80°C by simply replacing sodium with bulky imidazolium cation (figure 1).

Recently, inorganic polyoxometalate anions with the Keggin structure have been employed with sodium cations to synthesize room temperature ionic liquids.¹¹ Inorganic polyoxometalates are important class of solid acid catalytic materials with Brønsted

acidity.^{12–14} They contain Keggin anions such as XM₁₂O₄₀ⁿ⁻ (M = W, Mo; X = P, Si) with the primary structure shown in figure 1. The Keggin anions are interconnected by hydrogen-bonded water molecules (maximum 29) forming a secondary structure. These



(b) The Keggin unit

Figure 1. (a) 1-Butyl 3-methyl imidazolium bromide (BmImBr), and (b) PW₁₂O₄₀³⁻ Keggin molecular anion.

[†]Dedicated to Prof. C N R Rao on his 75th birthday

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large metal oxide framework anions (size ~ 1 nm) can react with variety of ionic liquids to form new ionic liquids^{7,11} and the corresponding organic–inorganic hybrid molecular materials.^{9,10} The molecular materials containing organic cations bonded with bulky Keggin anions can find applications, for example, in photochromism¹⁵ and electrochemical systems.^{16,17,18} In this paper, we report the synthesis and characterization of molecular hybrid compound based on imidazolium cation and polyoxometalate Keggin anion. The molecular nature, morphology and thermal stability of the hybrid compound are examined by PXRD, TGA, FTIR, UV-Vis-NIR DRS, ³¹P MAS NMR and SEM.

2. Experimental

2.1 Synthesis of 1-butyl 3-methyl imidazolium bromide (BmImBr) ionic liquid

All the starting materials were obtained from M/s Fluka and used as received. The ionic liquid, 1-butyl 3-methyl imidazolium bromide, was synthesized in the laboratory using reported procedure.¹⁹ The IL was prepared by taking 1 : 1 mole ratio of 1-methyl imidazole and 1-bromobutane. In a typical preparation, 33.29 g of liquid 1-bromobutane was added to 20 g of liquid 1-methyl imidazole in a round bottomed flask fitted with reflux condenser under stirring conditions at 80°C for 24 h. The top phase of the two phases formed contains unreacted starting material which can be removed by washing twice with ethyl acetate. This also ensures the removal of the unreacted material in the bottom phase containing IL product. The yellowish IL product of BmImBr liquid was further heated to 50°C to eliminate any dissolved ethyl acetate solvent and its formation was confirmed by IR, ¹H and ¹³C NMR.²⁰

2.2 Synthesis of 1-butyl 3-methyl imidazolium phosphotungstate

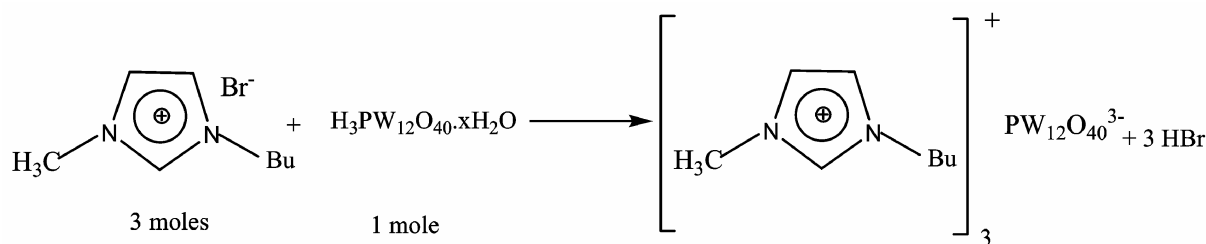
For the synthesis of 1-butyl 3-methyl imidazolium phosphotungstate salt, 1-butyl 3-methyl imidazolium bromide ionic liquid and aqueous solution of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) were taken in 3 : 1 mole ratio in order to prepare one mole of 1-butyl 3-methyl imidazolium phosphotungstate. 3 g of 1-butyl 3-methyl imidazolium bromide was added drop-wise to the solution containing 14.3 g of phosphotungstic acid (PWA) under constant stirring at room temperature. The white precipitate obtained (product in scheme 1) was washed with distilled water until bromine free (AgNO_3 test) and dried overnight at 80°C.

The CHN analysis of the white colour solid shows that one mole of Keggin anions of $\text{PW}_{12}\text{O}_{40}^{3-}$ react with 3 moles of 1-butyl 3-methyl imidazolium cations to form the hybrid molecular material (scheme 1). The product dissolves in DMSO but not in water.

2.3 Characterization

All samples were analysed by X-ray diffraction employing Shimadzu XD-D1 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The IR spectra of different samples (as KBr pellets) were recorded using Perkin–Elmer infrared spectrometer with a resolution of 4 cm^{-1} , in the range of $400\text{--}4000 \text{ cm}^{-1}$. Thermo gravimetric analysis (TGA) of IL-PWA hybrid material was conducted in pure N_2 gas (30 ml per minute) at a heating rate of 20°C per min on a Perkin-Elmer TGA-7 instrument.

The UV–Vis–NIR spectra were recorded in diffuse reflectance mode on Jasco V-570 UV-Vis NIR spectrophotometer equipped with an integrating sphere in the spectral range of 200–2500 nm. The spectra



Scheme 1.

are presented as Kubelka–Munk function ($F(R)$) versus incident photon wavelength. Scanning electron microscopy (SEM) images were taken using a FEI Quanta 200 microscope operating at 30 kV. The sample powders were deposited on a carbon tape before mounting on a sample holder.

The ^{31}P MAS NMR spectra of PWA and IL-PWA hybrid material were recorded using Bruker Avance 400 spectrometer at resonance frequency of 161.97 MHz for ^{31}P nuclei with Bruker CP MAS probe and the chemical shifts are reported in ppm (δ) relative to external 85 wt% H_3PO_4 . The ^{31}P MAS NMR spectra were recorded with a sample spinning rate of 8 kHz, and the delay between two pulses was 2 s for relaxation of the ^{31}P nuclei.

3. Results and discussion

3.1 Powder XRD study

In this work, we have substituted bulky anion $\text{PW}_{12}\text{O}_{40}^{3-}$ in place of Br^- in the imidazolium based ionic liquid template. The pairing of Keggin anion with imidazolium cation has led to the formation of organic–inorganic hybrid molecular solid. The formula estimated from the C–H–N elemental analysis of the sample is $\text{C}_{24.90}\text{H}_{41.93}\text{N}_{6.23}\text{PW}_{12}\text{O}_{40}$ which gives an empirical structure of $[(\text{C}_{8+x}\text{N}_2\text{H}_{15-y})_3][\text{PW}_{12}\text{O}_{40}]$. The surface area of this white colour non-porous solid is $2.8 \text{ m}^2 \text{ g}^{-1}$. Figure 2 shows the powder X-ray diffraction (PXRD) pattern of pure hydrated phosphotungstic acid and 1-butyl 3-methyl imidazolium phosphotungstate hybrid material, $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$. The phosphotungstic acid undergoes structural transformation where three acidic protons and most of the H_2O molecules are replaced by three 1-butyl 3-methyl imidazolium cations. The PXRD pattern of $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid material is quite complex and reveals different structure compared to pure PWA salt. The PXRD pattern suggests that the phosphotungstic acid secondary structure is modified by the 1-butyl 3-methyl imidazolium cations since most of the sandwiched water molecules in the form of H_3O^+ and H_5O_2^+ interacting with Keggin polyanions by hydrogen bonding are lost.¹² This type of host–guest interactions are known to bring about the structural transformations which are detected by powder X-ray diffraction.²¹ The intense peak at $2\theta = 9.4$ in the PXRD pattern seems to indicate that the compound may have layered type of structure.

3.2 FTIR study

The FTIR spectra are quite useful to find structural and bonding changes in the Keggin unit present in 1-butyl 3-methyl imidazolium phosphotungstate hybrid material, $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$. The parent $\text{PW}_{12}\text{O}_{40}^{3-}$ Keggin structure shows characteristic P–O stretching ($\sim 1083 \text{ cm}^{-1}$), $\text{W–O}_{\text{terminal}}$ stretching ($\sim 987 \text{ cm}^{-1}$), stretching of $\text{W–O}_e\text{–W}$ inter bridges between corner-sharing WO_6 octahedra ($\sim 891 \text{ cm}^{-1}$), stretching of $\text{W–O}_e\text{–W}$ intra bridges between edge-sharing WO_6 octahedra ($\sim 815 \text{ cm}^{-1}$) and P–O bending (596 cm^{-1}).^{13,14,22} In figure 3, the IR spectrum of IL-PWA is compared with the IR spectra of parent BmImBr and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$. The five prominent IR features due to $\text{PW}_{12}\text{O}_{40}^{3-}$ ion cluster in the hybrid material are clearly marked in the stretching region of $475\text{--}1120 \text{ cm}^{-1}$ indicating that the primary Keggin structure is intact in the 1-butyl 3-methyl imidazolium phosphotungstate material. As reported by

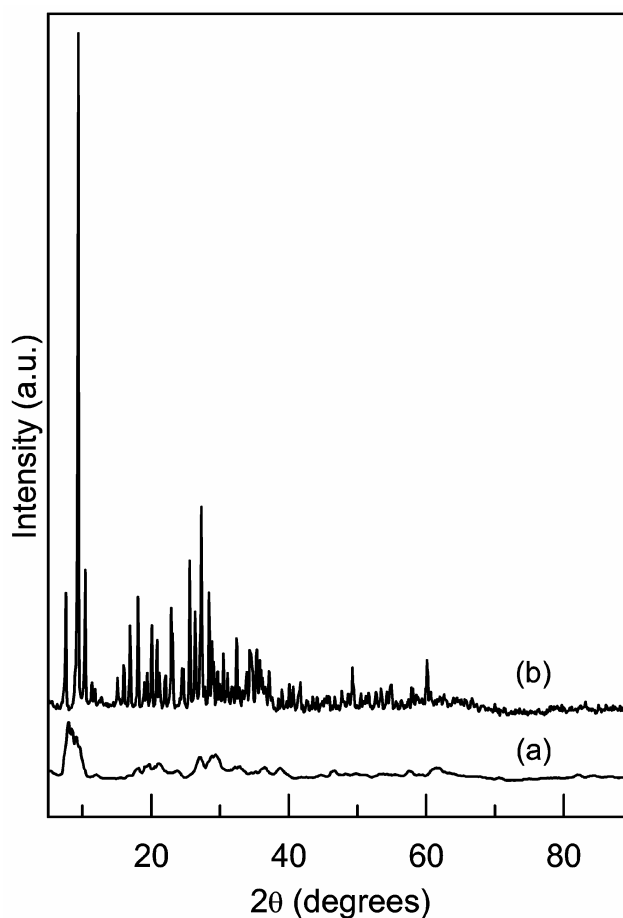


Figure 2. Powder XRD pattern of (a) $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, and (b) $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

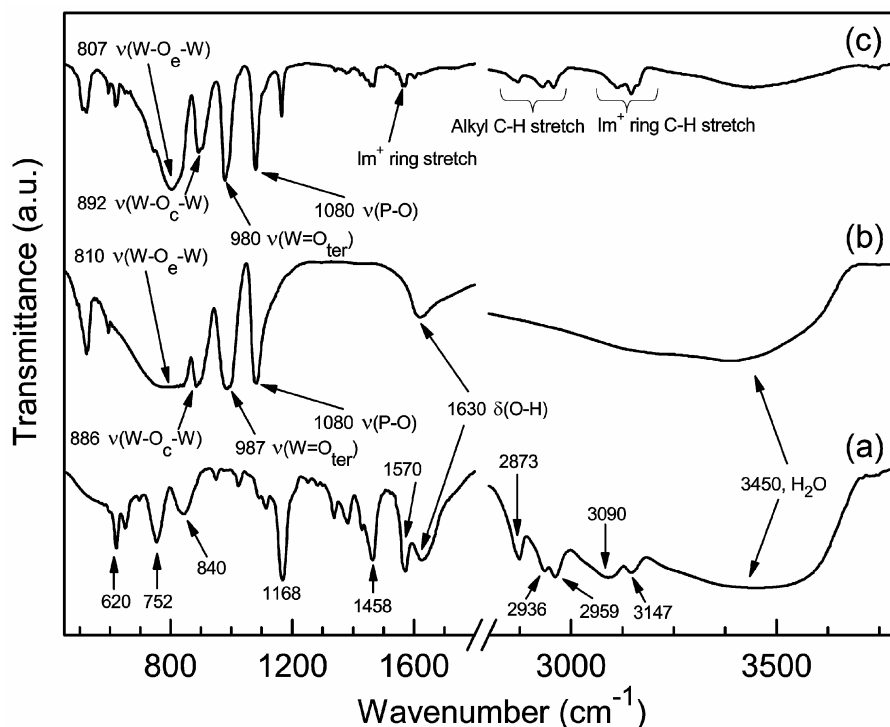


Figure 3. FTIR spectra of (a) 1-butyl 3-methyl imidazolium bromide (BmImBr) ionic liquid, (b) $\text{H}_3\text{PW}_{12}\text{O}_{40}/n\text{H}_2\text{O}$, and (c) $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

Table 1. IR data of BmImBr, $\text{H}_3\text{PW}_{12}\text{O}_{40}/n\text{H}_2\text{O}$ and $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

Wavenumber (cm^{-1})			Vibration mode
BmImBr	PWA	$[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$	
3450	3450	–	Water in the material
3146, 3090	–	3163, 3146, 3125, 3114, 3095	Imidazole ring $\nu(\text{C-H})$
2960, 2936, 2874	–	2960, 2936, 2874	Aliphatic $\nu(\text{C-H})$
1630	1630	–	O–H bending
1570, 1563	–	1570, 1563	Imidazole – $\nu(\text{ring})$
1168	–	1165	Imidazole H–C–C and H–C–N bending
–	1080	1080	$\nu(\text{P-O})$
–	987	980	$\nu(\text{W} = \text{O}_{\text{ter}})$
–	886	892	$\nu(\text{W-O}_e\text{-W})$
–	810	807	$\nu(\text{W-O}_e\text{-W})$
840	–	–	In-plane imidazole ring bending
752	–	–	Out-of-plane C–H bending of imidazole ring
650	–	620, 624	Imidazole $\text{C}_2\text{-N}_1\text{-C}_5$ bending

Wu *et al.*²⁰ BmIm^+ cation can be identified by the spectral features in the regions of $550\text{--}700\text{ cm}^{-1}$, $1130\text{--}1800\text{ cm}^{-1}$, $2800\text{--}3200\text{ cm}^{-1}$ and $3200\text{--}3800\text{ cm}^{-1}$ of the molecular compound (compare spectra (c) with (a) in figure 3). The IR peak assignments for the hybrid material containing 1-butyl 3-methyl imidazolium cations and $\text{PW}_{12}\text{O}_{40}^{3-}$ Keggin anions are given in table 1. The IR analysis clearly shows that

the basic structure and geometry of Keggin anion entrapped in the BmIm^+ cations are preserved in the hybrid molecular material but the water content (3450 cm^{-1}) is reduced significantly.²⁰

A closer examination of IR spectra in the imidazolium ring C–H stretch ($3000\text{--}3250\text{ cm}^{-1}$) and imidazolium ring stretch ($1500\text{--}1620\text{ cm}^{-1}$) in figure 4 reveals that there is a strong electrostatic interaction

between BmIm^+ cation and large Keggin anion. Due to this interaction, the two C–H stretching peaks of the imidazolium ring in BmImBr are split into five vibrational peaks in the $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular salt. The imidazolium ring vibration is also split with intensity variations (figure 3c). The origin of such C–H split is clearly attributed to specific interaction of BmIm cation with bulky Keggin anion.^{9,10} This type of interactions leading to C–H split have been reported in ionic compounds such as MPlm^+I_x .^{23–25}

3.3 TG analysis

The thermogravimetric behaviour of 1-butyl 3-methyl imidazolium phosphotungstate hybrid material is shown in figure 5. The TGA curve indicates weight loss regions at (i) 140 to 250°C, (ii) 250 to 420°C, (iii) above 420°C. The initial low temperature TG loss is due to small amounts of water present in the sample. The weight loss observed between 250 to 420°C is primarily due to the beginning of the decomposition of BmIm organic moiety. The pure

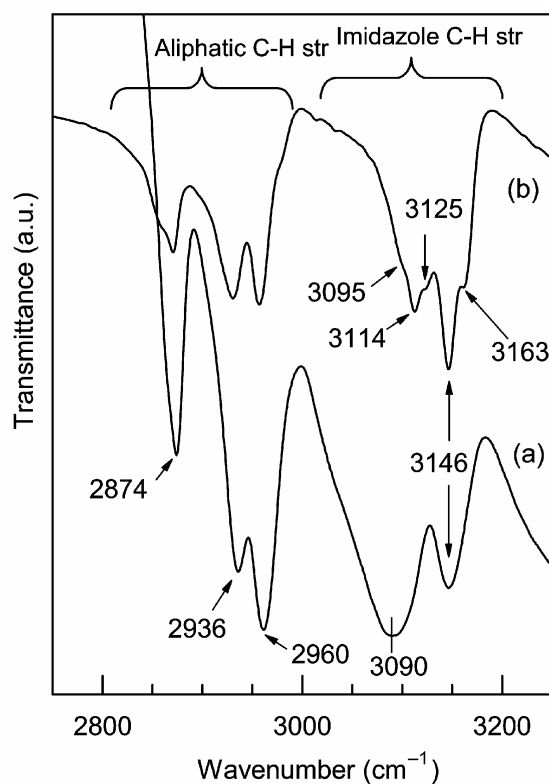


Figure 4. The C–H stretch region of (a) 1-butyl 3-methyl imidazolium bromide ionic liquid, (b) $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

PWA is known to decompose at 550°C,¹⁴ and the weight loss in TGA curve above 420°C indicates a shift in the decomposition temperature of the Keggin ions attached to imidazolium rings. The rapid weight loss above 420°C is mainly due to the decomposition of Keggin units to WO_3 and P_2O_5 . The thermal stability and also the Bronsted acidity of the Keggin units have been affected due to their interaction with BmIm^+ moieties in the molecular hybrid material.

3.4 UV-Vis DRS and ³¹P MAS NMR studies

The UV-Vis DR spectra of IL-PWA hybrid material recorded using integrating sphere are shown in figure 6. The heteropolyacids in their non-reduced form are generally characterized by oxygen-to-metal (O → M) charge transfer bands which appear in the UV region below 400 nm.^{9,10,14,15,26} When hybrid materials based on heteropolyacids are irradiated with UV light, electrons are excited from the low-energy electronic states (mainly oxygen 2p orbitals in heteropoly anions) to the high-energy states (mainly metal d orbitals). The electronic spectroscopy study of the phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}n\text{H}_2\text{O}$) shows three absorption bands at 220, 260 and 310 nm due to charge transfer transitions in the Keggin units (figure 6a) while BmImBr ionic liquid does not show any electronic transitions in the region (figure 6b). The absorption band at 220 nm is most likely to

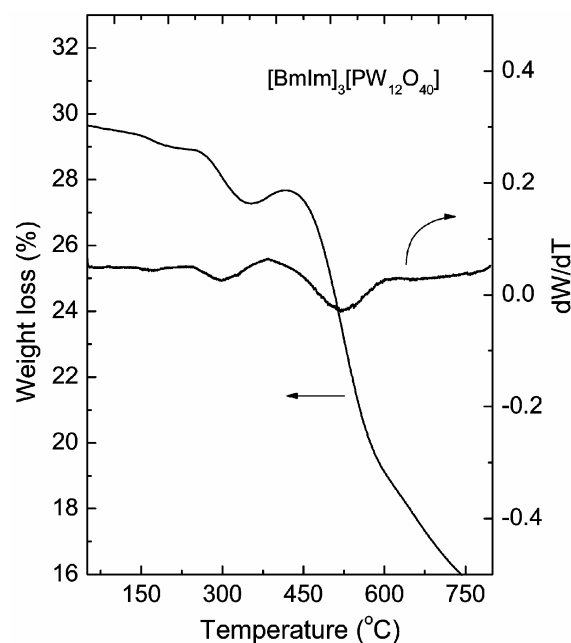


Figure 5. TGA of $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

be due to $O \rightarrow P$ transition. The other two absorption bands correspond to the ligand to metal charge transfer ($O^{2-} \rightarrow W^{6+}$) in the Keggin units, and interpreted as charge transfer absorptions where W atoms are located in $W-O_e-W$ intra bridges between edge-sharing WO_6 octahedra (260 nm), and $W-O_e-W$ inter bridges between corner-sharing WO_6 octahedra (310 nm).¹⁴ However, in the IL-PWA hybrid material the transition at 311 nm is shifted to 295 nm while the other two transitions remain at the same energy (figure 6c). This provides an evidence for the intermolecular electronic interactions between the 1-butyl 3-methyl imidazolium cations and the Keggin anion. There are no additional transitions seen in the DR spectrum of 1-butyl 3-methyl imidazolium phosphotungstate hybrid material since the compound is white, like its parent compound $H_3PW_{12}O_{40}nH_2O$.

Figure 7 shows the ^{31}P MAS NMR spectra of phosphotungstic acid and its hybrid material formed with ionic liquid. As reported, pure phosphotungstic acid shows a sharp and symmetric resonance peak at -15.1 ppm characteristic of phosphorous in the tetrahedral position of the Keggin unit.¹²⁻¹⁴ This resonance peak has been shifted to -11.5 ppm in the IL-PWA hybrid material which is again a clear indica-

tion of strong interaction between 1-butyl 3-methyl imidazolium cation and Keggin anions in the compound. The ^{31}P chemical shift is consistent with the UV-Vis DRS result discussed earlier. However, the downfield shift in ^{31}P MAS NMR of phosphotungstic acid can also occur due to the loss of water molecules from bulk material.¹² This aspect is discerned clearly in near IR study in the next section.

3.5 Near IR study and SEM study

Near IR spectroscopy is used to detect water content in $H_3PW_{12}O_{40}nH_2O$ and IL-PWA hybrid material by studying overtones and combination bands of the fundamental stretching frequencies of H_2O .^{9,10,27,28} The near IR spectra of parent $H_3PW_{12}O_{40}nH_2O$ and the IL-PWA hybrid materials are recorded by diffuse reflectance mode in the range of 1200 to 2500 nm, which are shown in figure 8. The three prominent bands observed at 1462, 1956 and 2252 nm in the near IR spectrum show the presence of water and hydroxyl groups in $H_3PW_{12}O_{40}nH_2O$. These bands are attributable to the first overtone of hydroxyl groups, ($2\nu_{O-H}$), combination band corresponding to hydroxyl stretching and bending, ($\nu_{O-H} + \delta_{H_2O}$), and

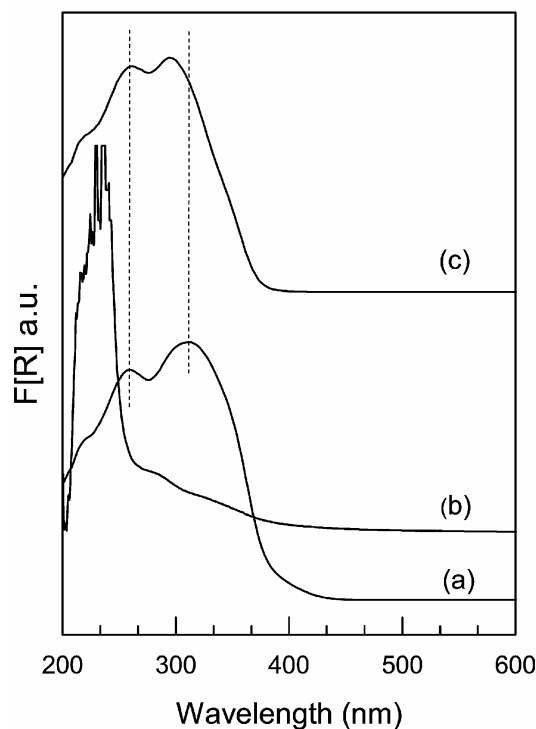


Figure 6. UV-Vis DR spectra of (a) $H_3PW_{12}O_{40}nH_2O$, (b) BmImBr solution, and (c) $[BmIm]_3[PW_{12}O_{40}]$ hybrid molecular material.

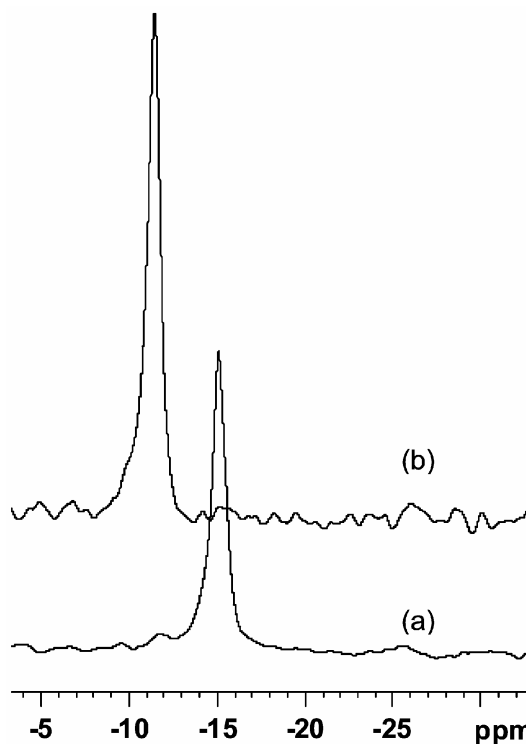


Figure 7. ^{31}P MAS NMR spectra of (a) $H_3PW_{12}O_{40}nH_2O$, and (b) $[BmIm]_3[PW_{12}O_{40}]$ hybrid molecular material.

combination band of ($\nu_{\text{O-H}} + \delta_{\text{O-H}}$) vibrational modes, respectively. All these characteristic overtones and combination bands due to H_2O are absent in the IL-

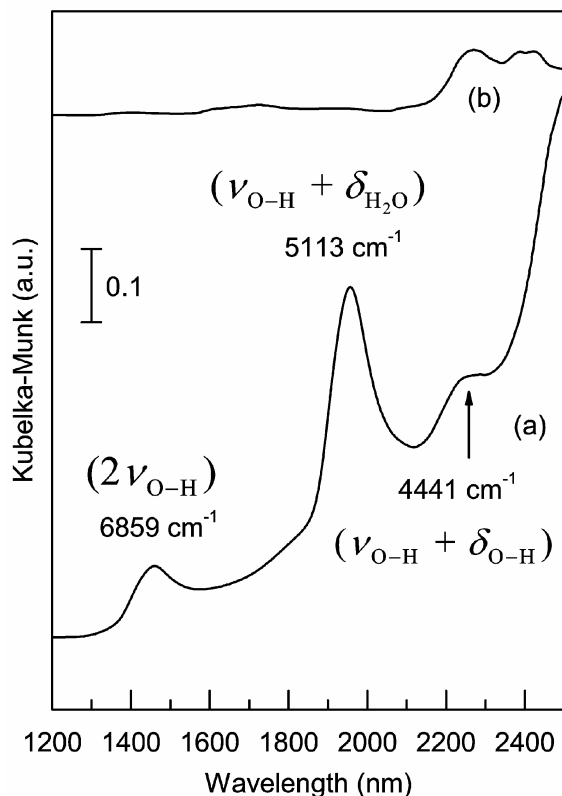


Figure 8. Near IR spectra of (a) $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, and (b) $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

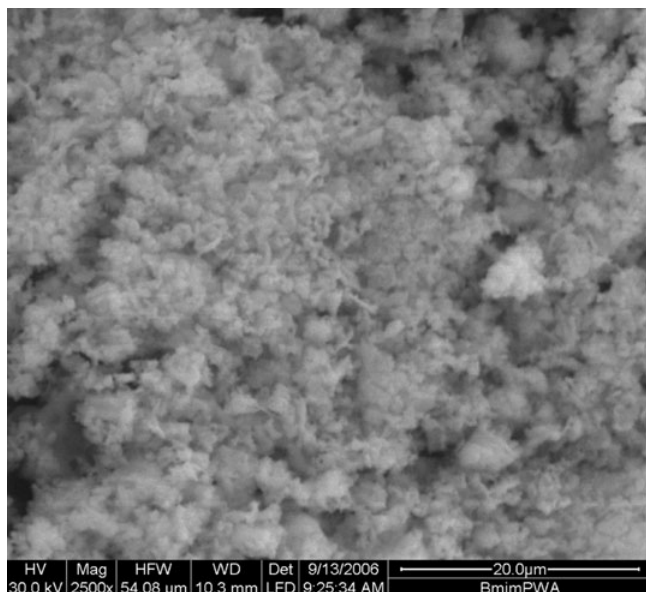


Figure 9. SEM image of $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid molecular material.

PWA hybrid material (figure 8b). The characteristic IR peak at 1620 cm^{-1} due to water is also very weak in the IR spectrum of the hybrid material (figure 3c). This confirms the elimination of water molecules associated with PWA when reacted with the BmIm cations forming the IL-PWA hybrid molecular material.

The morphology of the hybrid material has been studied by SEM and the image obtained for 1-butyl 3-methyl imidazolium phosphotungstate hybrid material at $2500 \times$ magnification is shown in figure 9. The SEM topography of the powder reveals clusters of irregular shape and thread-like particles of about micron size present in the sample.

4. Conclusions

The $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid material formed by the reaction between 1-butyl 3-methyl imidazolium bromide ionic liquid and phosphotungstic acid has been fully investigated. This is a solid material with melting point $\sim 400^\circ\text{C}$. IR spectrum shows the presence of both 1-butyl 3-methyl imidazolium cations and Keggin anions. The spectral shifts in UV-Vis DRS and ^{31}P MAS NMR, and the ring C-H split in IR confirm strong interactions between the organic moiety and the Keggin species in the material. The hybrid material is hydrophobic and has no water content as determined by the near IR spectra.

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