

# Increasing the efficiency of flame retardant polypropylene catalyzed by polyoxometalate based ionic liquid

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## 1. Experimental section

### 1.1 Materials

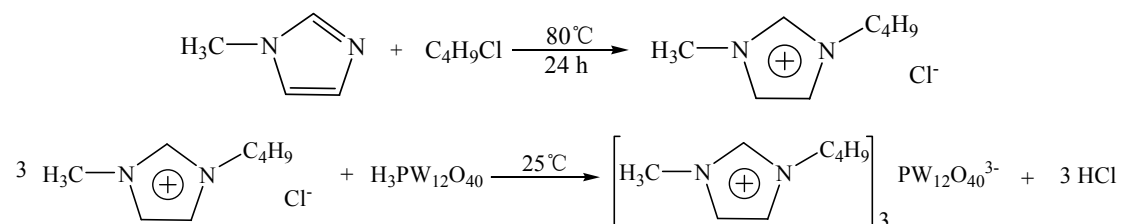
APP ( $n > 1500$ ) was supplied by Presafer (Qingyuan, China) Phosphor Chemical Company Limited. PER was purchased from Aladdin Industrial Inc. (Shanghai, China). The PP resin (F401) was obtained Yangzi Oil Co., with a melt index of 2.0 g/min (230 °C/2.16 kg). The reagents 1-methyl imidazole (MIm) was obtained from Sinopharm Chemical Reagent Co., Ltd. 12-phosphomolibdic acid (Chemical formula:  $H_3PMo_{12}O_{40} \cdot nH_2O$ , abbreviated as PMoA) and 1-chlorobutane of analytical purity were purchased from Aladdin Reagent Chemical Factory. The IFR used in this work is a mixture of APP/PER with a weight ratio 3:1. All reagents were used as received from commercial sources without further purification.

### 1.2. Synthesis of polyoxometalate based ionic liquid

The synthesis of 1-butyl-3-methyl imidazolium chloride ([BMIm]Cl) ionic liquid (IL) was carried out by taking 1:1 molar ratio of 1-methyl imidazole and 1-chlorobutane at 80 °C for 24 h in nitrogen atmosphere. After recrystallization from ethyl acetate, the intermediate product [BMIm]Cl was obtained<sup>1</sup>. The [BMIm]PMo was synthesized by [BMIm]Cl and PMoA at 3:1 mole ratio. Firstly, 0.47 g [BMIm]Cl and 1.82 g PMoA were dissolved in deionized water, respectively, then mixed together under constant stirring for 12 h. Then a green precipitate was formed. The product was filtered and washed for several times with deionized water until chloride-free ( $AgNO_3$  aqueous test). Finally, the obtained products were dried

overnight at 80 °C in a oven.

The processing of this [BMIm]PMo is shown in Scheme S1.



**Scheme S1** Processing of synthesizing [BMIm]<sub>3</sub>PMo

### 1.3 Preparation of PP composites

PP composites were prepared by melt-blending on a Brabender mixer at 200 °C with roller speed 50 rpm for 10 min. After mixing, the samples were hot-pressed at about 200 °C under 10 MPa for 3 min into sheets in the dimensions of 100.0 mm × 100.0 mm × 3.2 mm and then cut into suitable sample bars for LOI and UL-94 testing.

### 1.4 Characterization

Thermal gravimetric analysis (TGA) experiments were performed on a Mettler Toledo TGA/DSC1 Analyzer. About 5 mg specimens were heated from 25 °C to 800 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere (50 mL/min).

DSC measurement was carried out using a Mettler Toledo DSC. About 5-10 mg specimens were heated from 25 °C to 300 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere (50 ml/min).

Limiting oxygen index (LOI) was measured by a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM D2863-97. The specimens used for the test were 100.0 mm × 6.5 mm × 3.2 mm in dimension.

UL-94 vertical tests were performed on an AG5100B vertical burning tester (Zhuhai Angui Testing Equipment Company, China). The specimens' size was 100.0 mm × 13 mm × 3.2 mm according to ASTM D3801.

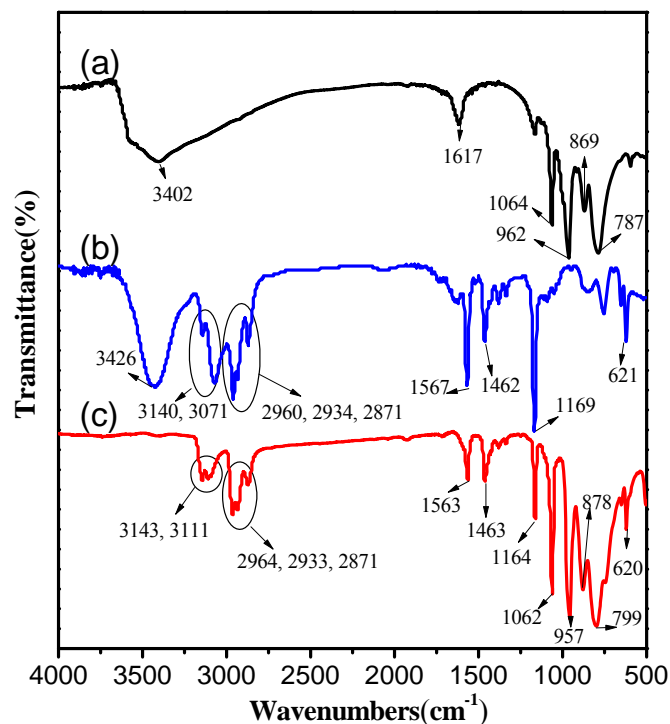
FT-IR spectra for different samples were recorded with a Nicolet FT-IR spectrometer using KBr pellets.

<sup>1</sup>H NMR spectra were recorded with a 400MHz AMX NMR spectrometer using DMSO-*d*<sub>6</sub> as solvent.

## 2. Structure and properties of [BMIm]<sub>3</sub>PMo

### 2.1 FT-IR spectra

FT-IR is used to identify structural and bonding changes in the Keggin unit presented in polyoxometalate and polyoxometalate ionic liquid. The FT-IR spectra of PMoA, [BMIm]Cl and [BMIm]<sub>3</sub>PMo are shown in Fig.S1, and the characteristic peaks and their corresponding vibration modes are gathered in Table S1.



**Fig S1.** FT-IR spectra of (a) PMoA, (b) [BMIm]Cl, and (c) [BMIm]<sub>3</sub>PMo

Fig. S1 (a) shows the FT-IR of PMoA, and the main characteristic peaks of the Keggin structure are found, for example 1064 cm<sup>-1</sup> (P-O stretching), 962 cm<sup>-1</sup> (Mo-O<sub>ter</sub> stretching), 869 cm<sup>-1</sup> (stretching of Mo-O<sub>c</sub>-Mo inter bridges between corner-sharing MoO<sub>6</sub> octahedra), and 787 cm<sup>-1</sup> (stretching of Mo-O<sub>c</sub>-W intra bridges between edge sharing MoO<sub>6</sub> octahedra)<sup>2</sup>. These peaks shift to 1062 cm<sup>-1</sup>, 957 cm<sup>-1</sup>, 878 cm<sup>-1</sup> and 799 cm<sup>-1</sup> in the [BMIm]<sub>3</sub>PMo (Fig. S1 (c)), respectively, indicating the reaction from PMoA to [BMIm]<sub>3</sub>PMo. In addition, Fig. S1 (b) and (c) show the characteristic peaks at 3143–2871 cm<sup>-1</sup> (C-H stretching in the imidazole ring), 1563–1462 cm<sup>-1</sup> (imidazole ring stretching), 1169–1164 cm<sup>-1</sup> (imidazole H-C-C and

H–C–N bending), 745-754  $\text{cm}^{-1}$  (out of plane C–H bending of imidazole ring), and 620  $\text{cm}^{-1}$  (imidazole C–N–C bending). The peaks at 3402–3426  $\text{cm}^{-1}$  (water) are disappeared in Fig. S1 c. Analysis of the FT-IR data shows that the basic structure and geometry of the Keggin anions entrapped in the [BMIm]<sup>+</sup> cations are preserved but the water content is significantly reduced in the hybrid material.

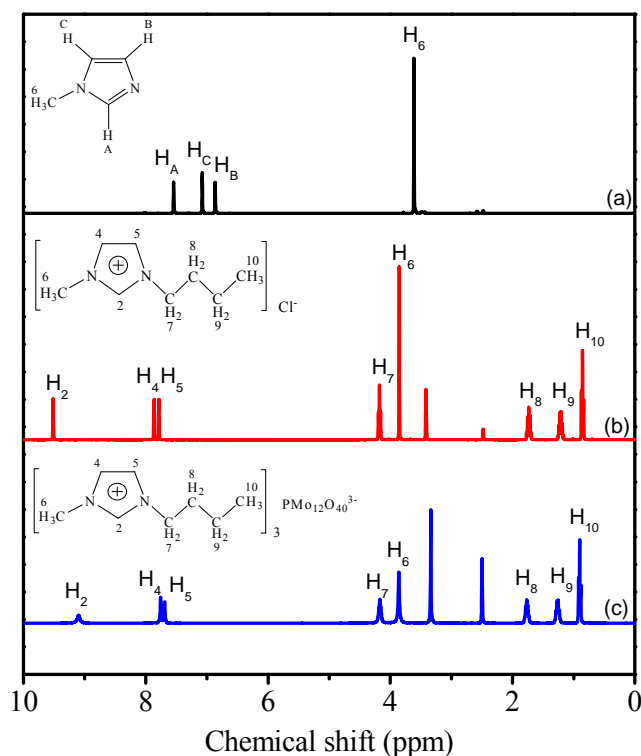
**Table S1** FT-IR bands of [BMIm]Cl, PMoA and [BMIm]<sub>3</sub>PMo<sup>4,3</sup>

Wavenumbers/ $\text{cm}^{-1}$			Vibration mode
PMoA	[BMIm]Cl	[BMIm] <sub>3</sub> PMo	
3402	3426	-	Water in the material
-	3140,3071	3143,3111	Imidazole ring (C-H str.)
-	2960, 2934,2871	2964, 2933, 2871	Aliphatic (C-H str.)
1617	1623	-	O-H bending
-	1567	1563	Imidazole – ring str.
-	1462	1463	Imidazole – ring str.
-	1169	1164	Imidazole H-C-C and H-C-N bending
1064	-	1062	P-O str.
962	-	957	Mo=O str.
869	-	878	$\nu$ (Mo-O <sub>c</sub> -Mo)
787	-	799	$\nu$ (Mo-O <sub>e</sub> -Mo)
-	754	745	Out of plane imidazole C-H bending
-	621	620	Imidazole C-N-C bending

## 2.2 NMR analysis

Fig. S2 shows <sup>1</sup>H-NMR spectrum of the MIm, [BMIm]Cl and [BMIm]<sub>3</sub>PMo, and the chemical shift of the protons are listed in Table S2. As shown in Fig. S2 (a), the resonances at 7.55, 7.08 and 6.87 ppm can be attributed to three protons bonded to the imidazole ring, and the resonance at 3.61 ppm can be assigned to the methyl proton. The anions have great effect on the chemical shift of the protons bonded to the imidazole ring directly. Fig. S2 (b) shows that the resonances of these protons bonded to imidazole ring in MIm shift to higher position due to the loss of a electron and the formation of imidazolium chloride. As shown in Fig. S2 (c), the replacement of

chloride anion by phosphomolybdate anion leads to the lower chemical position of protons in the imidazole structure than that in [BMIm]Cl. The chemical shift of other C-H change slightly. Analysis of the  $^1\text{H-NMR}$  spectrum also proves the formation of [BMIm] $_3$ PMo.



**Fig S2.**  $^1\text{H}$  NMR spectra of a) MIm, b) [BMIm]Cl, and c) [BMIm] $_3$ PMo

**Table S2** HNMR data of MIm, [BMIm]Cl, and [BMIm] $_3$ PMo

$^1\text{HNMR}$	MIm $\Delta$	[BMIm]Cl $\delta$	[BMIm] $_3$ PMo $\delta$
H <sup>2</sup> imidazole	s 7.55 (H <sub>A</sub> )	s 9.52	9.10
H <sup>4</sup> imidazole	s 7.08 (H <sub>C</sub> )	s 7.86	7.76
H <sup>5</sup> imidazole	s 6.87 (H <sub>B</sub> )	s 7.79	7.69
N-CH <sub>2</sub>		t 4.18	4.17
N-CH <sub>3</sub>	s 3.61	s 3.85	3.86
Water peak		s 3.42	3.34
Solvent peak		s 2.48	2.50
N-CH <sub>2</sub> CH <sub>2</sub>		m 1.74	1.76

N-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	m 1.23	1.27
N-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	t 0.86	0.90

### 2.3 DSC analysis

Though the [BMIm]Cl is liquid at room temperature. After reaction with PMoA, its melting point is increased to 183 °C. It is well known that the melting point of PP is 160-170 °C. The processing temperature of PP is 180-200 °C usually. So the [BMIm]<sub>3</sub>PMo is liquid during processing which is easier to be dispersed uniformly in PP composites than solid state.

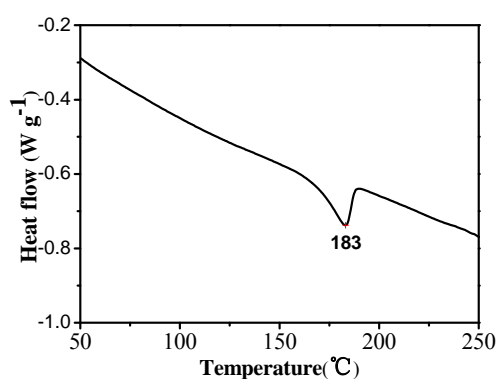


Fig. S3 DSC trace of [BMIm]<sub>3</sub>PMo

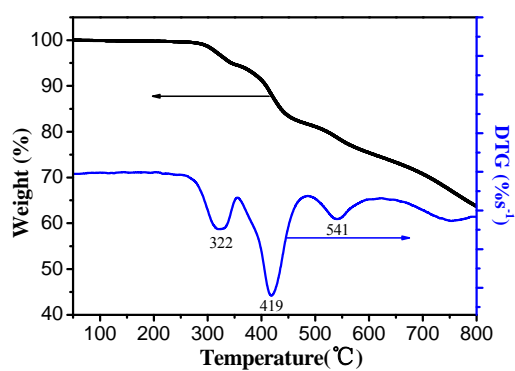


Fig. S4 TGA and DTG curves of [BMIm]PMo

### 2.4 TGA

Fig. S4 is the TGA and DTG curves of the [BMIm]PMo. The 1 wt% thermal decomposition temperature ( $T_{1wt\%}$ ) of [BMIm]<sub>3</sub>PMo is 293 °C, indicating the organic part (BMIm cation) begins to decompose. The processing temperature of PP is 180-200 °C. So it can meet the requirement of PP composites. At a higher temperature, besides the decomposition of the organic part, the Keggin anion also decomposes to be MoO<sub>3</sub> oxide phases, leading to a significant decrease in the weight. From DTG, it is found that the first decomposition peak is at 322 °C. The second peak at 419 °C may be assigned to the collapse, which is 90 °C higher than [BMIm]Cl.<sup>1</sup> As shown in the report of Ngo et al, ILs with non-halide anion dramatically improve the thermal stability with the onset decomposition occurring almost 100 °C above the corresponding ILs with halide anion.<sup>5</sup> Therefore, this increase is caused mainly by the polyoxometalate anion.

## Reference

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