

## Supporting Information

### Polyoxometalate-based Protic Alkylimidazolium Salts as Reaction- Induced Phase-Separation Catalyst for Olefin Epoxidation

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#### General remarks

A Perkin Elmer Pyris Diamond was used in the current study for the thermogravimetric analysis (TGA) measurements. A constant heating rate of 10°C min<sup>-1</sup> and high-purity nitrogen purge (100 mL min<sup>-1</sup>) were used for all the measurements. The ionic liquid samples were dried under vacuum for two hours before conducting the TGA measurements. The standard material used for calibrating the equipment was  $\alpha$ -sapphire powder (Perkin Elmer). The XRD analysis were performed in D/MAX 2550 VB/PC using a graphite crystal as monochromator.

#### The XRD analysis

The XRD patterns of the parent potassium peroxotungstate  $K_2[W_2O_{11}]$  and its liquid derivatives  $[HDIm]_2[W_2O_{11}]$  and  $[DMIm]_2[W_2O_{11}]$  are shown in Figure S1. The bottom reveals the crystalline state of the  $K_2[W_2O_{11}]$ , and the above two corresponding to the derivatives reveal their amorphous state, which is consistent with the liquid state properties of the samples.<sup>1</sup>

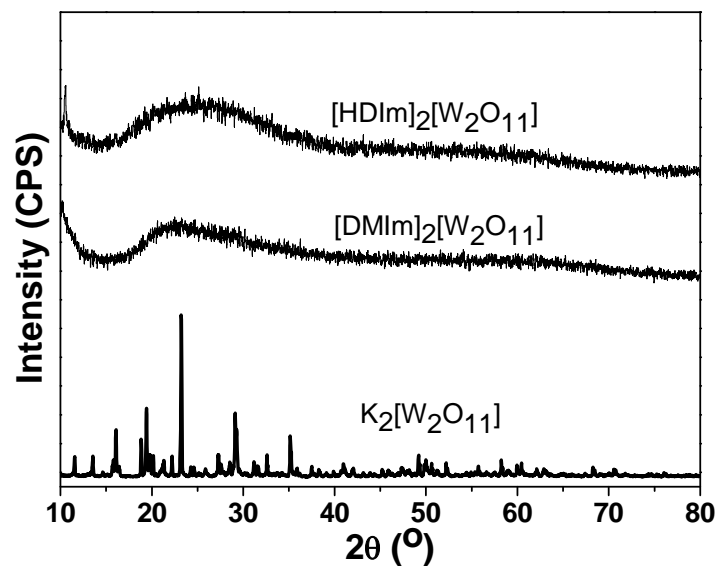
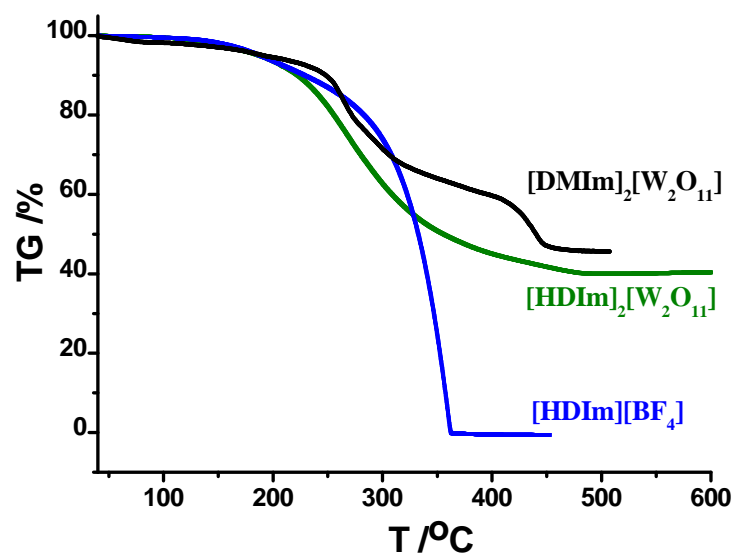


Figure S1. XRD patterns of the parent potassium peroxotungstate  $K_2[W_2O_{11}]$  and its liquid derivatives  $[HDIm]_2[W_2O_{11}]$  and  $[DMIm]_2[W_2O_{11}]$

### TG–DTA analysis

The thermal stability of the ILs  $[HDIm][BF_4]$ ,  $[HDIm]_2[W_2O_{11}]$  and  $[DMIm]_2[W_2O_{11}]$  were investigated by using TGA method (heating rate: 10°C/min; N<sub>2</sub> flow, 100 mL/min). As shown in Figure S2, the IL  $[HDIM][BF_4]$  was thermally stable below 320°C, its onset decomposing temperature was around 319°C and almost decomposed completely at 360°C, which are in agreement with the previous report.<sup>2</sup> In comparison, the functionalized ILs  $[HDIM]_2[W_2O_{11}]$  and  $[DMIm]_2[W_2O_{11}]$  gave slightly higher thermal stability, and the remaining part can be attributed to the anion part as tungsten oxides.



**Figure S2.** TGA curves for [HDIIm]<sub>2</sub>[W<sub>2</sub>O<sub>11</sub>], [DMIm]<sub>2</sub>[W<sub>2</sub>O<sub>11</sub>] and [HDIIm][BF<sub>4</sub>].

### References

- [1] A. B. Bourlino, K. Raman, R. Herrere, Q. Zhang, L. A. Archer and E. P. Giannelis, *J. Am. Chem. Soc.*, 2004, **126**, 15358–15359.
- [2] W. H. Awad and J. W. Gilman, *Thermochim Acta*, 2004, **409**, 3–11.