# ESI (Electronic Supplementary Information)

# Substitution effect in reversible gel-liquid phase transformation polyoxometalate ionic liquid compounds

**Xuefei Wu,[a] Huaxue Cai,[a] Qingyin Wu,*[a] and Wenfu Yan[b]**

[a] *Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China. Fax: +86 571 87951895; Tel: +86 571 88914042;*

*E-mail: qywu@zju.edu.cn (Q.Y. Wu)*

[b] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, PR China.*

## Instruments and reagents

Inductively coupled plasma (ICP-MS) analysis was determined on a Shimadzu V-1012 ICP-MS spectrometer. Infrared (IR) spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer over the wave number range 400–4000 $cm^{-1}$ using KBr pellet. The thermal stability of the sample was investigated using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) techniques from room temperature to 600 °C. TG-DTA measurement was conducted on a SHIMADZU thermal analyzer in a Nitrogen stream, with a heating rate of 10 $°C \cdot min^{-1}$. Conductivity was measured by a DDS-11A conductivity meter fitted with a Shanghai DJS-1 and DJS-10 electrode. The conductivity meter was calibrated by the standard KCl solution with a concentration of 0.1 $mol \cdot L^{-1}$. The cell constant was 0.88. The cyclic voltammetric studies were conducted on CHI650C electrochemical workstation in dimethyl formamide (DMF). The density of substrate was 0.25mM and 0.2M $NaClO_4$ was assigned as supporting electrolyte. The working electrode was glass carbon which is 5mm in diameter and the counter electrode was Pt. The surfaces of electrodes were pretreated to fresh before experiment. The reference electrode was saturated calomel electrode. The solution was deaerated by nitrogen before experiment.

All reagents were analysis grade.

**Table S1** The assignment of the vibration modes in the IR spectra of the complexes and the pure acids

| Vibrations | Wavenumber ($cm^{-1}$) | | | |
|---|---|---|---|---|
| | $H_8P_2W_{16}V_2O_{62}$ | $[MIMPS]_8P_2W_{16}V_2O_{62}$ | $[MIMPS]_6H_2P_2W_{16}V_2O_{62}$ | $[MIMPS]_4H_4P_2W_{16}V_2O_{62}$ |
| O-H stretching | 3416 | 3423 | 3435 | 3427 |
| H-O-H bending | 1620 | 1634 | 1640 | 1632 |
| $-CH_2$ scissoring | - | 1471 | 1461 | 1461 |
| $-CH_2$ twisting | - | 1389 | 1394 | 1394 |
| S=O bending | - | 1229 | 1223 | 1240 |
| S=O bending | - | 1169 | 1170 | 1171 |
| $P-O_a$ stretching | 1089 | 1075 | 1081 | 1082 |
| $M-O_d$ stretching | 968 | 961 | 949 | 957 |
| $M-O_b-M$ stretching | 909 | 896 | 913 | 908 |
| $M-O_c-M$ stretching | 783 | 792 | 795 | 789 |