

# Redox Chemistry of Ruthenium ions in Mono-substituted Keggin Tungstophosphate: A New Synthetic Extension for Ruthenium Derivatives based on $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{VI}}\text{N}]^{4-}$

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**Figure S1.** Different color of (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2], (n-Bu<sub>4</sub>N)<sub>4</sub>[3].

**Figure S2** <sup>31</sup>P NMR spectra of reaction solution of (n-Bu<sub>4</sub>N)<sub>4</sub>[1] under irradiation for 0, 35, 95, 180 min and the <sup>31</sup>P NMR spectrum of (n-Bu<sub>4</sub>N)<sub>4</sub>[2] in range from -2 to -34 ppm.

**Figure S3.** X-ray photoelectron spectra for N 1s, O 1s and W 4f, Cl 2p in (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2], (n-Bu<sub>4</sub>N)<sub>4</sub>[3].

**Figure S4** The ESI mass spectrum of compound (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2] and (n-Bu<sub>4</sub>N)<sub>4</sub>[3] in acetonitrile.

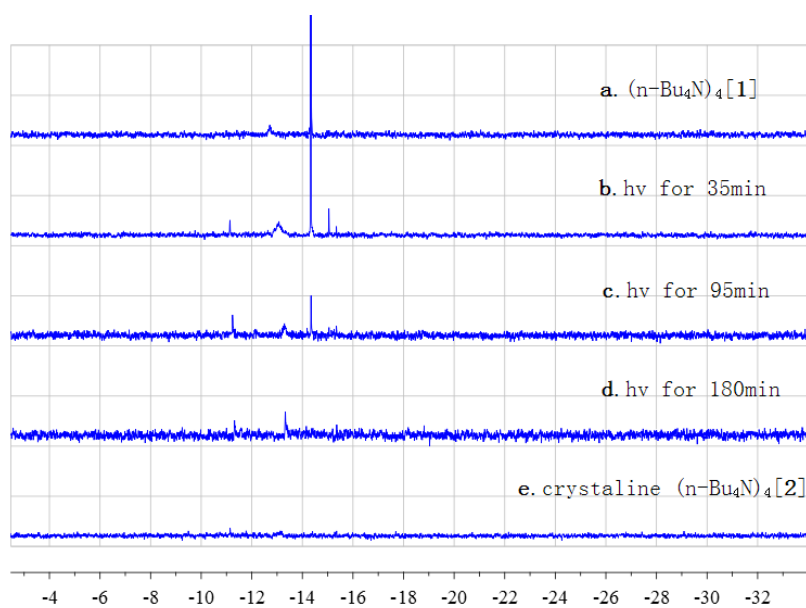
**Figure S5** UV-vis spectra of (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2], (n-Bu<sub>4</sub>N)<sub>4</sub>[3] in CH<sub>3</sub>CN.

**Figure S6** Thermogram of the (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2] and (n-Bu<sub>4</sub>N)<sub>4</sub>[3]

**Figure S1.** Different color of  $(n\text{-Bu}_4\text{N})_4[1]$ ,  $(n\text{-Bu}_4\text{N})_4[2]$ ,  $(n\text{-Bu}_4\text{N})_4[3]$ .

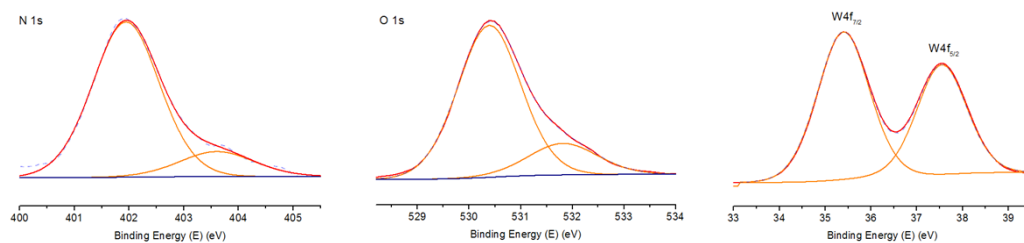


**Figure S2**  $^{31}\text{P}$  NMR spectra of reaction solution of  $(\text{n-Bu}_4\text{N})_4[\mathbf{1}]$  under irradiation for 0, 35, 95, 180 min and the  $^{31}\text{P}$  NMR spectrum of  $(\text{n-Bu}_4\text{N})_4[\mathbf{2}]$  in range from -2 to -34 ppm.

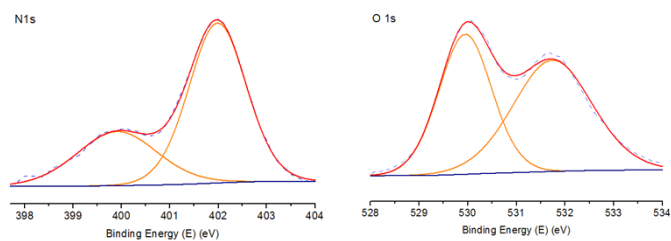


**Figure S3.** X-ray photoelectron spectra for N 1s, O 1s and W 4f, Cl 2p in (n-Bu<sub>4</sub>N)<sub>4</sub>[**1**], (n-Bu<sub>4</sub>N)<sub>4</sub>[**2**], (n-Bu<sub>4</sub>N)<sub>4</sub>[**3**].

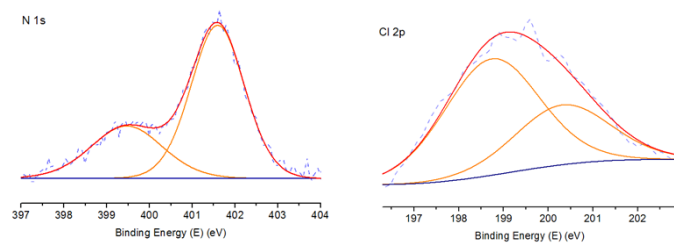
a) N 1s, O 1s and W 4f for (n-Bu<sub>4</sub>N)<sub>4</sub>[**1**]



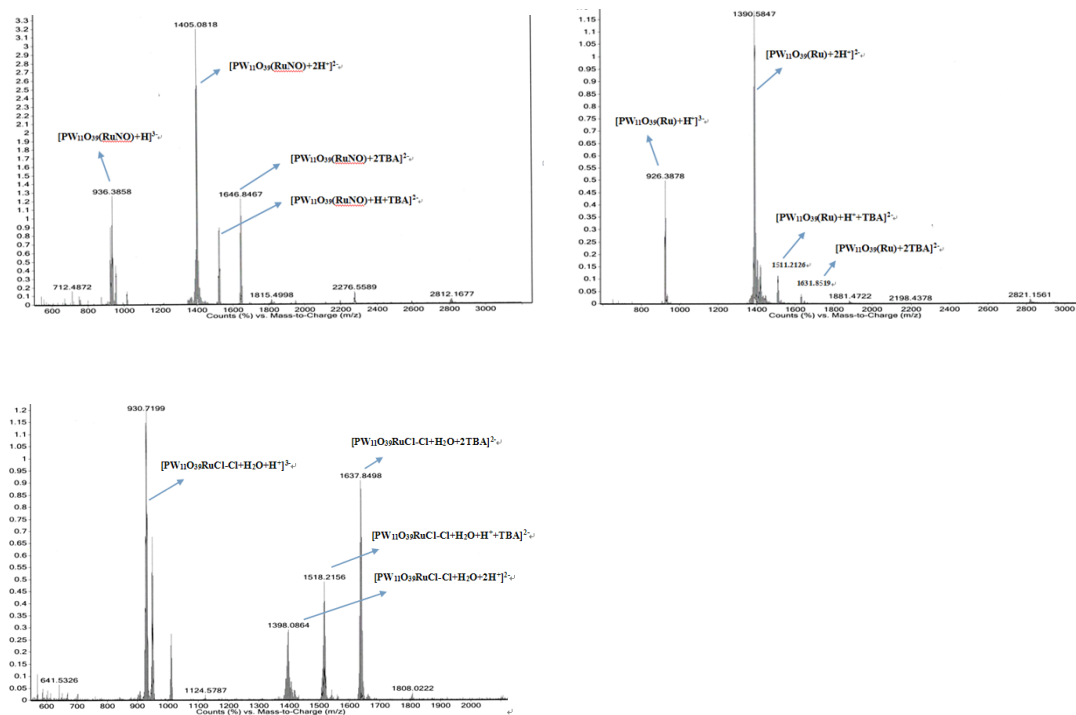
b) N 1s and O 1s for (n-Bu<sub>4</sub>N)<sub>4</sub>[**2**]



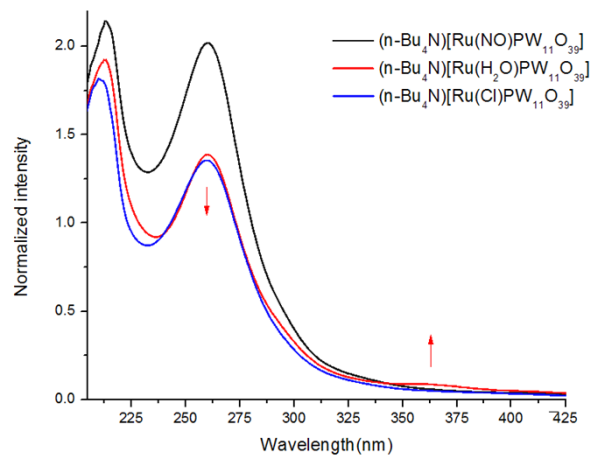
c) N 1s and Cl 2p for (n-Bu<sub>4</sub>N)<sub>4</sub>[**3**]



**Figure S4** The ESI mass spectrum of compound (n-Bu<sub>4</sub>N)<sub>4</sub>[**1**], (n-Bu<sub>4</sub>N)<sub>4</sub>[**2**] and (n-Bu<sub>4</sub>N)<sub>4</sub>[**3**] in acetonitrile.



**Figure S5** UV-vis spectra of  $(n\text{-Bu}_4\text{N})_4[1]$ ,  $(n\text{-Bu}_4\text{N})_4[2]$ ,  $(n\text{-Bu}_4\text{N})_4[3]$  in  $\text{CH}_3\text{CN}$ .



**Figure S6** Thermogram of the (n-Bu<sub>4</sub>N)<sub>4</sub>[1], (n-Bu<sub>4</sub>N)<sub>4</sub>[2] and (n-Bu<sub>4</sub>N)<sub>4</sub>[3]

