SUPORTING INFORMATION MATERIAL

for

Synthesis of Metal-Substituted Tetraalkylphosphonium Polyoxometalate Ionic Liquids

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Fig. S1. – Picture of \((\text{THTP})_4[(\text{PW}_{11}\text{O}_{39}\text{Mn}^{III}\text{(H}_2\text{O})])\) 3 after heated with the flask tilted and then with the flask back again in a vertical position.

Fig. S2. – UV-vis spectra of (A) \((\text{THTP})_4[(\text{PW}_{11}\text{O}_{39}\text{Fe}^{III}\text{(H}_2\text{O})])\) 1; (B) \((\text{THTP})_5[(\text{PW}_{11}\text{O}_{39}\text{Co}^{II}\text{(H}_2\text{O})])\) 2; (C) \((\text{THTP})_4[(\text{PW}_{11}\text{O}_{39}\text{Mn}^{III}\text{(H}_2\text{O})])\) 3 in methanol and acetonitrile, respectively \((C = 1.0 \times 10^{-3}\text{M}).\)
Fig. S3. – $^1$H NMR spectra, in dmso-$d_6$, of (A) THTPBr, (B) (THTP)$_4$[(PW$_{11}$O$_{39}$)Fe$^{III}$(H$_2$O)] 1, (C) (THTP)$_2$[(PW$_{11}$O$_{39}$)Co$^{II}$(H$_2$O)] 2 and (D) (THTP)$_4$[(PW$_{11}$O$_{39}$)Mn$^{III}$(H$_2$O)] 3. (*) indicates an impurity found on the tube.

Fig. S4. – $^{31}$P NMR spectrum of (THTP)$_5$[(PW$_{11}$O$_{39}$)Co$^{II}$(H$_2$O)] 2 in dmso-$d_6$.

Fig. S5. – FTIR-ATR spectra of (A) (THTP)$_2$[PW$_{11}$O$_{39}$] (4) and (B) (THTP)$_6$[P$_2$W$_{20}$O$_{70}$] (5).
Fig. S6. – Thermal analyses performed on (A) (THTP)$_5$[PW$_{11}$O$_{39}$Co$^{II}$H$_2$O]$_2$ and (B) (THTP)$_4$[PW$_{11}$O$_{39}$Mn$^{III}$H$_2$O]$_3$. In I, the thermogravimetric curves are presented and in II, the DSC curves.

Fig. S7. – DSC plots for (A) (THTP)$_5$[PW$_{11}$O$_{39}$Co$^{II}$H$_2$O]$_2$; (B) (THTP)$_4$[PW$_{11}$O$_{39}$Mn$^{III}$H$_2$O]$_3$, between -100 °C and +30 °C. Heating rate: -10 °C·min$^{-1}$. 

4
Fig. S8. – X-ray patterns for (A) (THTP)$_4$[PW$_{11}$O$_{39}$Fe$^{III}$]$_1$(H$_2$O)$_1$; (B) (THTP)$_4$[PW$_{11}$O$_{39}$Co$^{II}$]$_2$(H$_2$O)$_2$, between -100 °C and +25 °C. Heating rate: -5 °C·min$^{-1}$.

Fig. S9. – Variation of the electrochemical signal of (1) for a pH 2.0 solution. (A) cyclic voltammograms for $v = 5, 10, 20, 25, 50, 75, 100, 200, 250$ and $500$ mV s$^{-1}$; (B) slopes of $(\iota_\text{p}) = \delta (\log v)$ for the Fe$^{III}$/Fe$^{II}$ and the first W$^{VI}$/W$^{V}$ redox pairs for scanning rates between 10 and 100 mV s$^{-1}$. 