# SUPORTING INFORMATION MATERIAL

*for*

## Synthesis of Metal-Substituted Tetraalkylphosphonium Polyoxometalate Ionic Liquids

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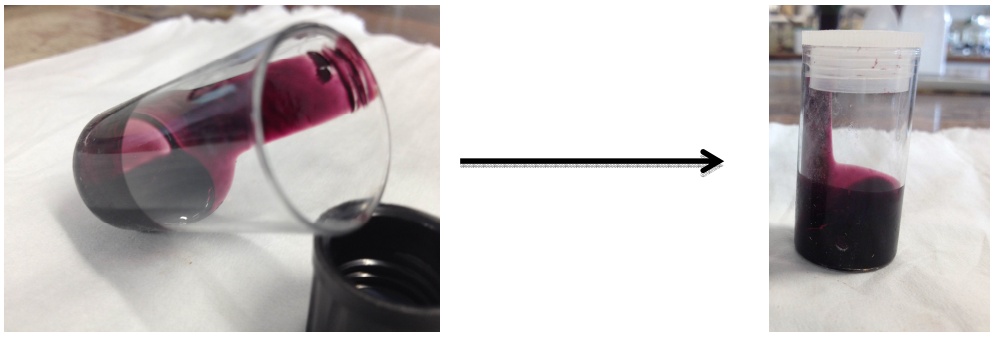

**Fig. S1. – Picture of $(THTP)_4[(PW_{11}O_{39}Mn^{III}(H_2O)]$ 3 after heated with the flask tilted and then with the flask back again in a vertical position.**

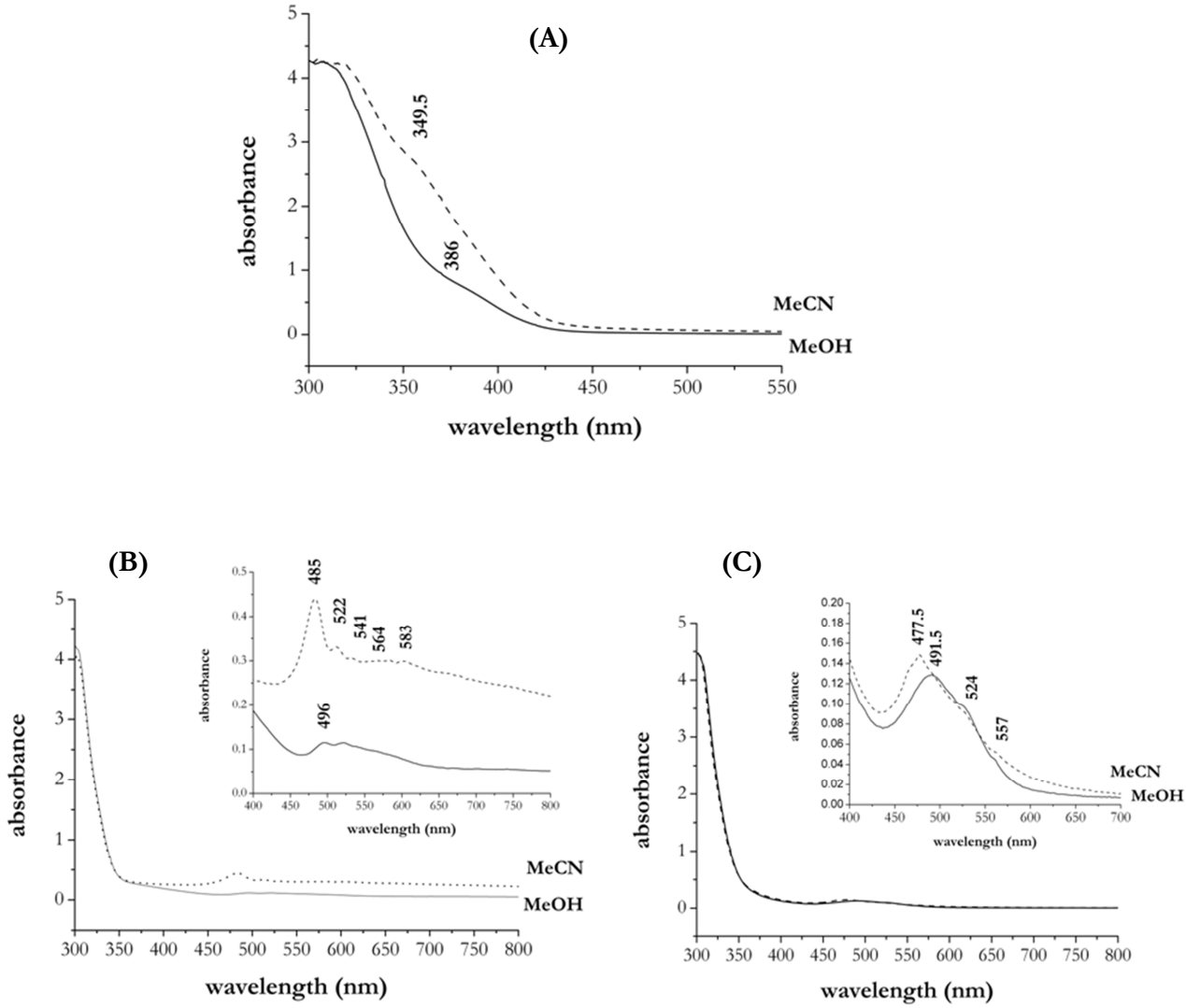


**Fig. S2. – UV-vis spectra of (A) $(THTP)_4[PW_{11}O_{39}Fe^{III}(H_2O)]$ 1; (B) $(THTP)_5[(PW_{11}O_{39}Co^{II}(H_2O)]$ 2; (C) $(THTP)_4[(PW_{11}O_{39}Mn^{III}(H_2O)]$ 3 in methanol and acetonitrile, respectively ($C$ = 1.0 x $10^{-3}$M).**

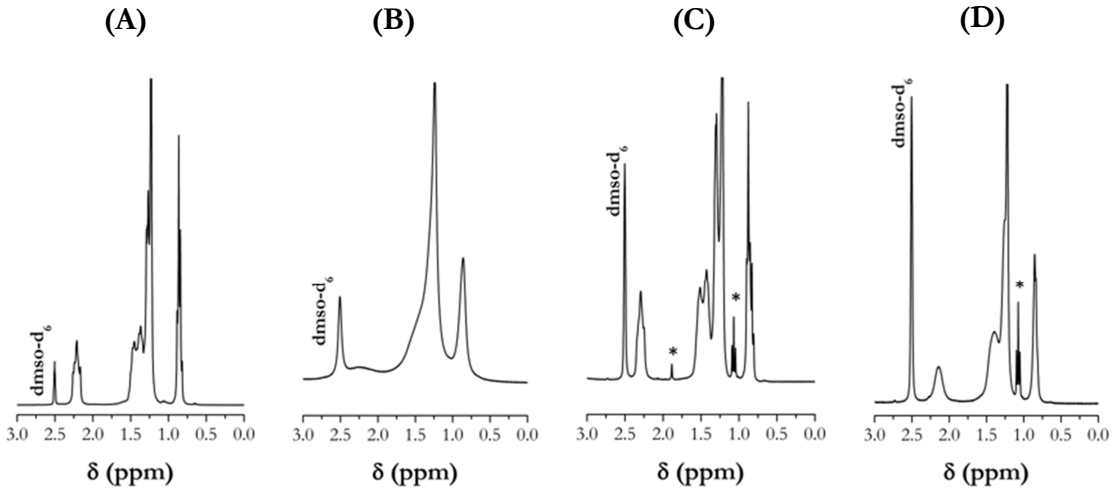


**Fig. S3. – $^{1}$H NMR spectra, in dmso-d$_6$, of (A) THTPBr, (B) (THTP)$_4$[(PW$_{11}$O$_{39}$Fe$^{III}$(H$_2$O)] 1, (C) (THTP)$_5$[(PW$_{11}$O$_{39}$Co$^{II}$(H$_2$O)] 2 and (D) (THTP)$_4$[(PW$_{11}$O$_{39}$Mn$^{III}$(H$_2$O)] 3. (*) indicates an impurity found on the tube.**

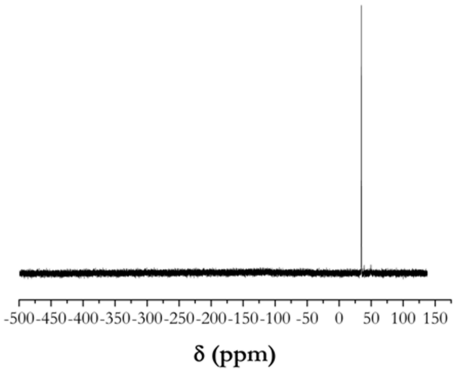


**Fig. S4. – $^{31}$P NMR spectrum of (THTP)$_5$[(PW$_{11}$O$_{39}$Co$^{II}$(H$_2$O)] 2 in dmso-d$_6$.**

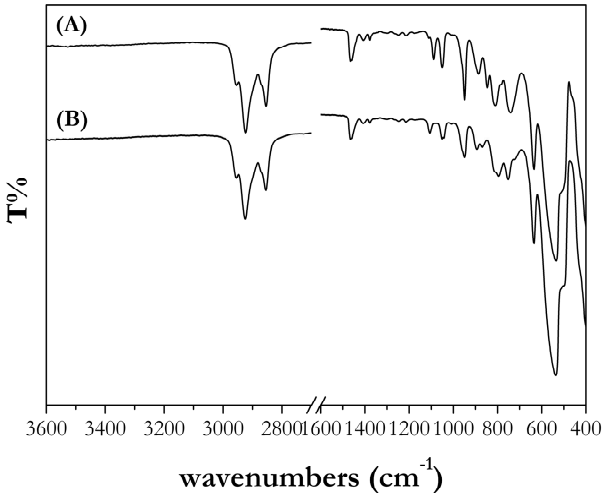


**Fig. S5. – FTIR-ATR spectra of (A) (THTP)$_7$[PW$_{11}$O$_{39}$] (4) and (B) (THTP)$_{10}$[P$_2$W$_{20}$O$_{70}$] (5).**

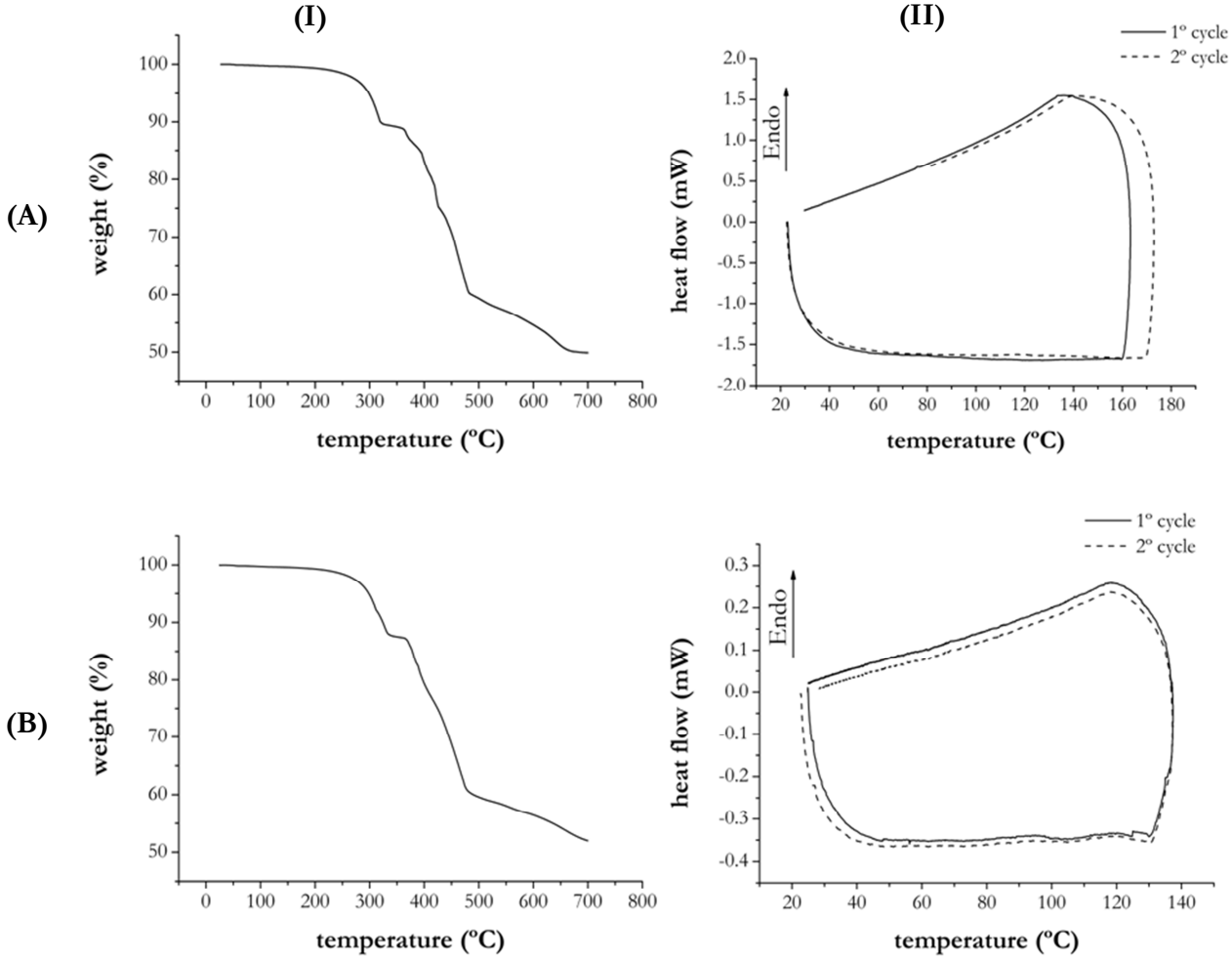


**Fig. S6. – Thermal analyses performed on (A) $(THTP)_5[PW_{11}O_{39}Co^{II}(H_2O)]$ 2 and (B) $(THTP)_4[PW_{11}O_{39}Mn^{III}(H_2O)]$ 3. In I, the thermogravimetric curves are presented and in II, the DSC curves.**

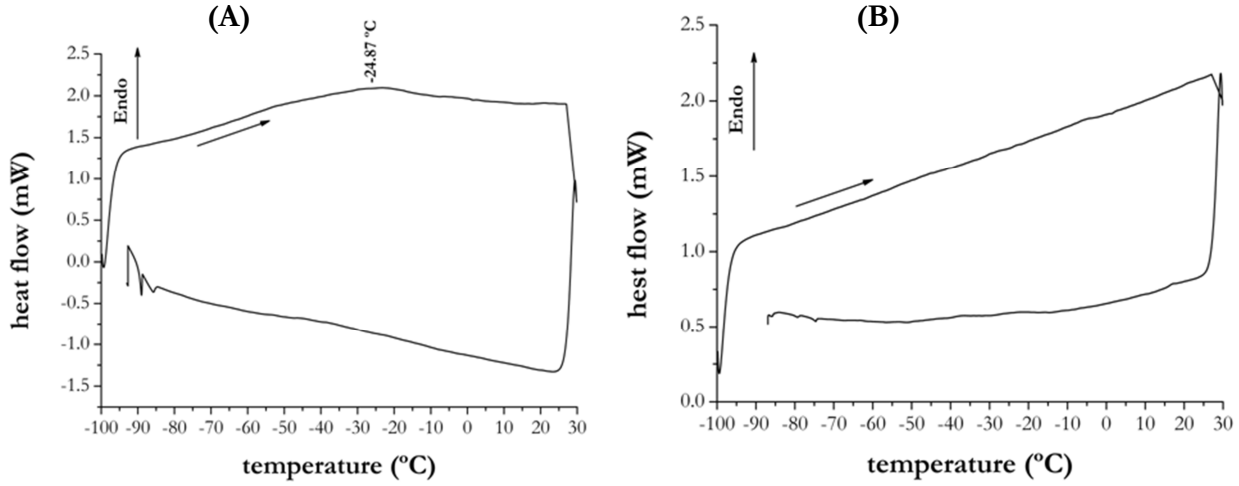


**Fig. S7. – DSC plots for (A) $(THTP)_5[PW_{11}O_{39}Co^{II}(H_2O)]$ 2; (B) $(THTP)_4[PW_{11}O_{39}Mn^{III}(H_2O)]$ 3, between -100 ºC and +30 ºC. Heating rate: -10 ºC· min$^{-1}$.**

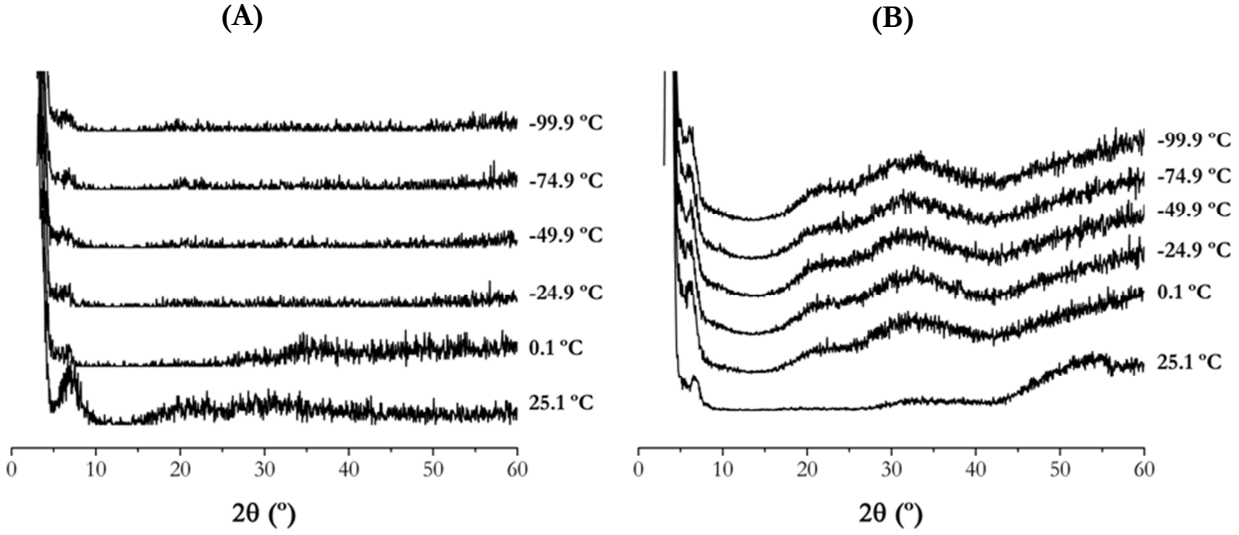


**Fig. S8. – X-ray patterns for (A) $(THTP)_4[PW_{11}O_{39}Fe^{III}(H_2O)]$ 1; (B) $(THTP)_5[(PW_{11}O_{39}Co^{II}(H_2O)]$ 2, between -100 ºC and +25 ºC. Heating rate: -5 ºC·min$^{-1}$.**

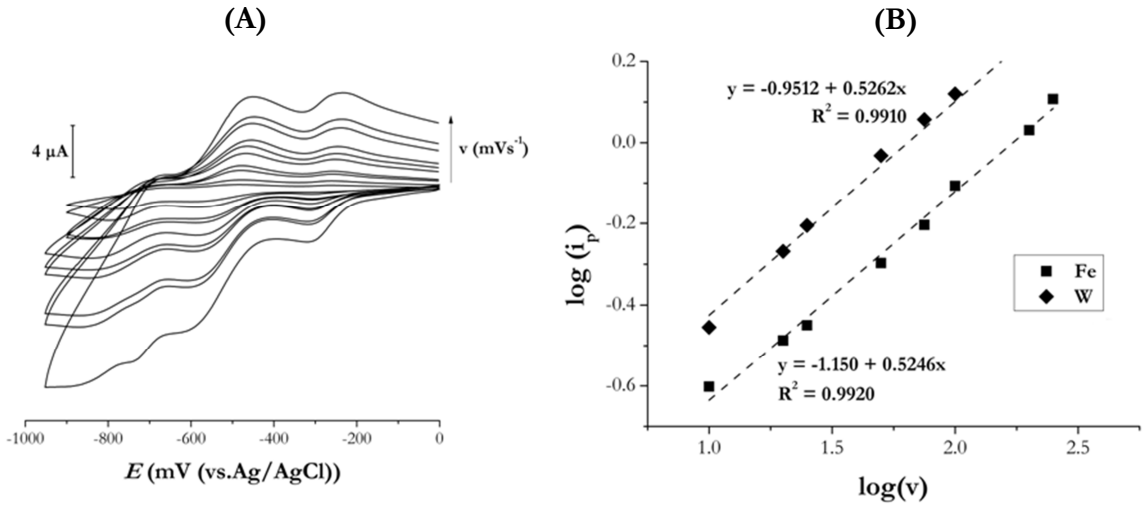


**Fig. S9. – Variation of the electrochemical signal of (1) for a pH 2.0 solution. (A) cyclic voltammograms for v = 5, 10, 20, 25, 50, 75, 100, 200, 250 and 500 mV s$^{-1}$; (B) slopes of ($i_p$) = $f$(log v) for the $Fe^{III}/Fe^{II}$ and the first $W^{VI}/W^{V}$ redox pairs for scanning rates between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