

Supporting Information

An α -Keggin Polyoxometalate Completely Constructed From The Late Transition Metal Co^{II} As Poly Atom

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Synthesis of $[\text{Co}_{20}(\text{OH})_{24}(\text{MMT})_{12}(\text{SO}_4)](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1): A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.146g, 0.5mmol), MMT (0.066g, 0.5mmol), triethylamine (0.102g, 1.67mmol), ethanolamine (0.036g, 0.359mmol), 2ml H_2O and 2ml $\text{C}_2\text{H}_5\text{OH}$ was sealed in a 23 ml Teflon-lined stainless steel vessel and heated to 110°C for 3 days and then cooled to room temperature at a rate of $0.1^\circ\text{C} \cdot \text{min}^{-1}$. Pink octahedral crystals were obtained. The product was washed with $\text{C}_2\text{H}_5\text{OH}$, and dried in air (36% yield based on Co^{II}). Elemental analysis (%) calcd for $\text{C}_{36}\text{H}_{72}\text{N}_{26}\text{Co}_{20}\text{O}_{40}\text{S}_{25}$: C, 12.39; H, 2.07; N, 10.44; S, 22.94. Found: C, 12.36; H, 2.10; N, 10.46; S, 22.91.

A Typical Procedure for styrene Polymerization: In a 100ml flask that was equipped with a magnetic stir bar, catalyst **1** (55 g, 4.5 μmol) and styrene (22.60 g, 217 mmol) was added immediately. The mixture was stirred at room temperature for 2.5 days. The resulting colorless solution gradually became viscous. Addition of methanol precipitated poly(styrene), which after filtration was dried at 60°C overnight and weighted (3.4 g, 12.6 kg of PS/(mol Cat·h)).

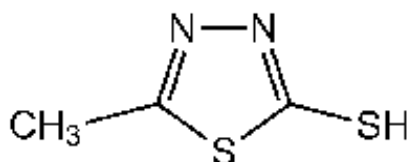


Figure S1. The structure of MMT.

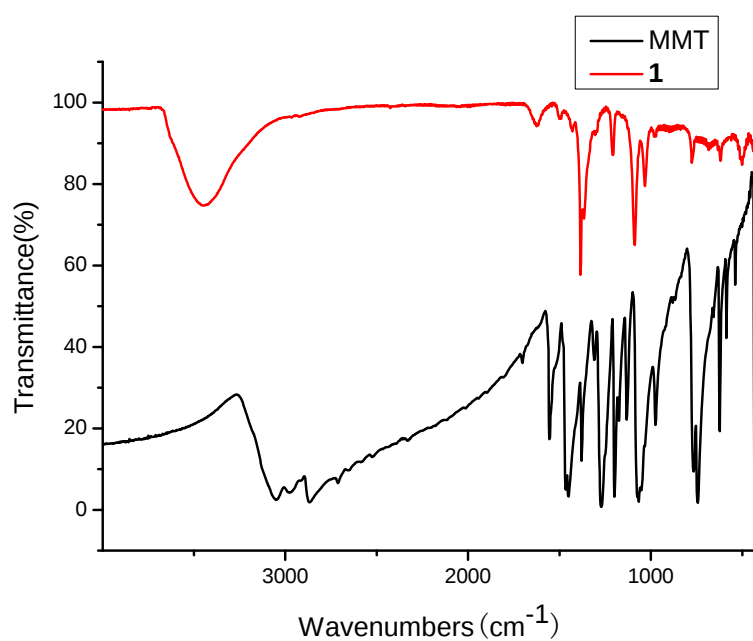


Figure S2. The IR spectrum of MMT and **1**.

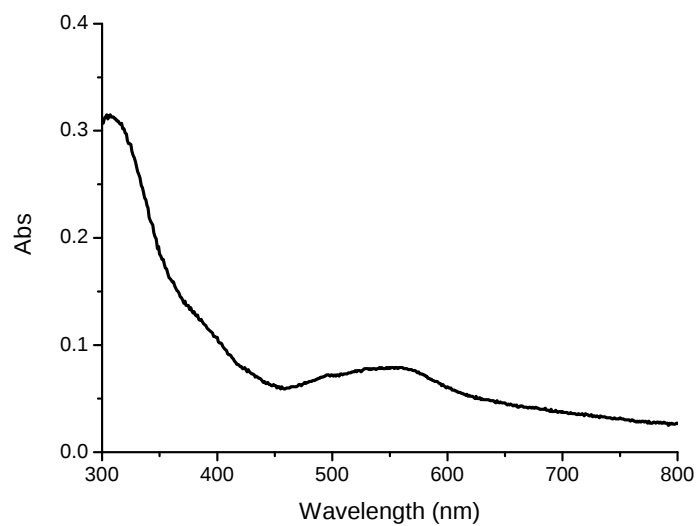


Figure S3. Solid state UV-vis spectra of **1**.

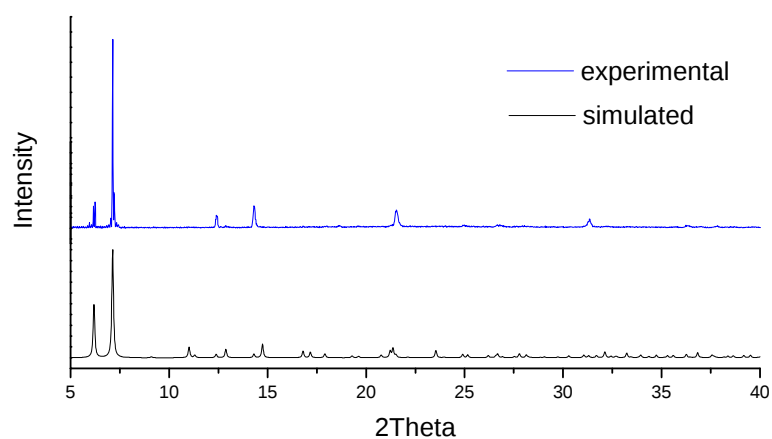


Figure S4. The PXR D spectrum of **1**.

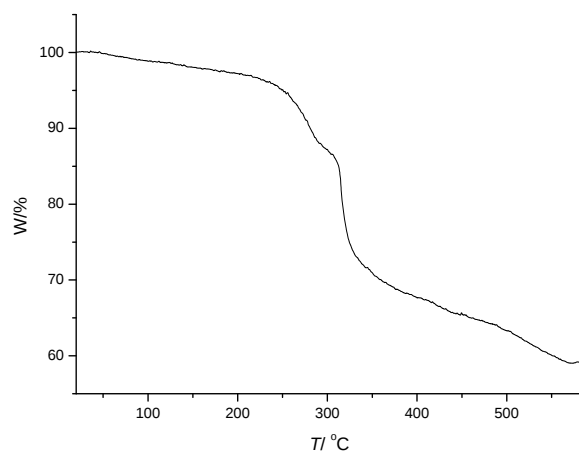


Figure S5. The TGA profile of **1** in the range of 20°C – 600°C in N_2 .

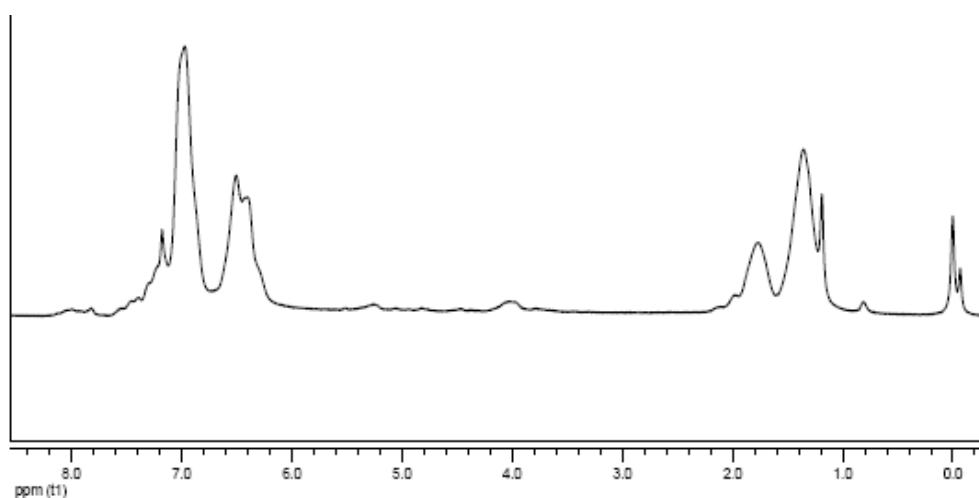


Figure S6. The ^1H NMR spectrum of aPS obtained by cluster **1**.

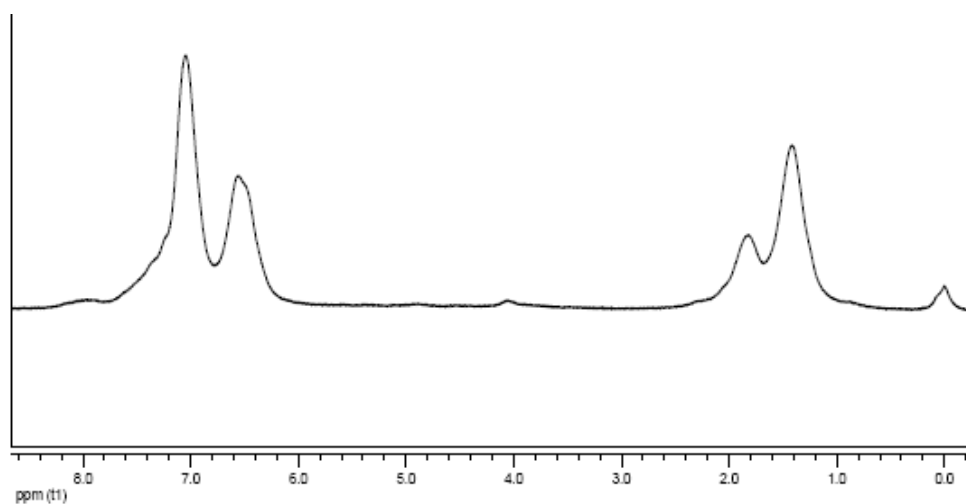


Figure S7. The ^1H NMR spectrum of aPS obtained by cluster **1c**.

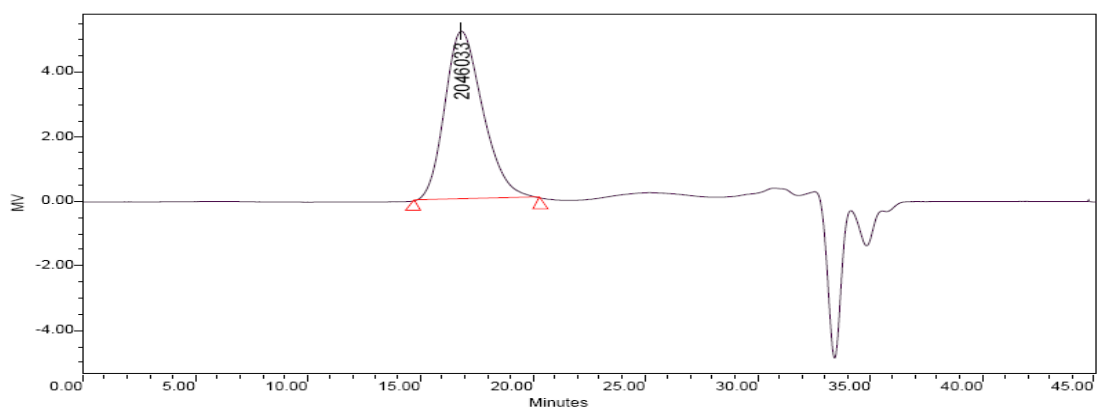


Figure S8. The GPC curve of aPS obtained by cluster **1**.

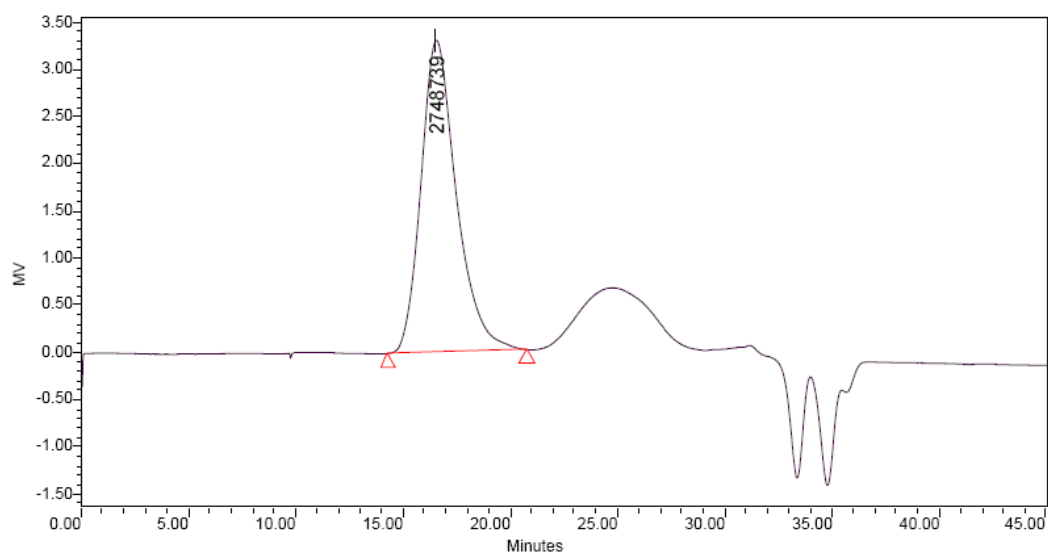


Figure S9. The GPC curve of aPS obtained by cluster **1c**.

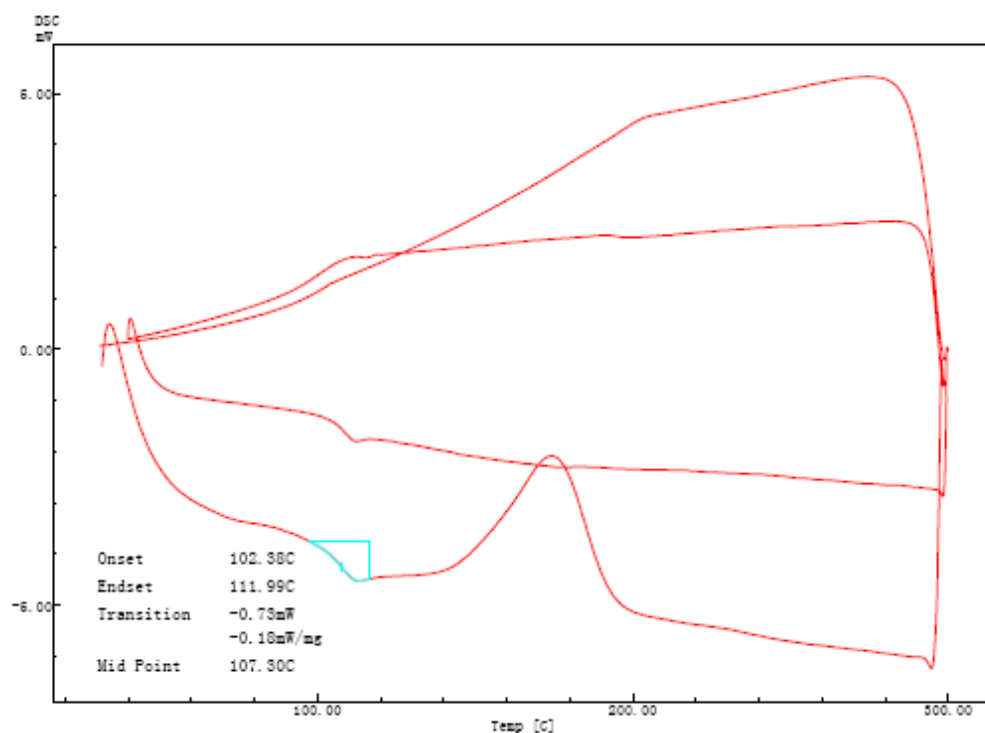


Figure S10. The DSC curve of aPS obtained by cluster **1**.

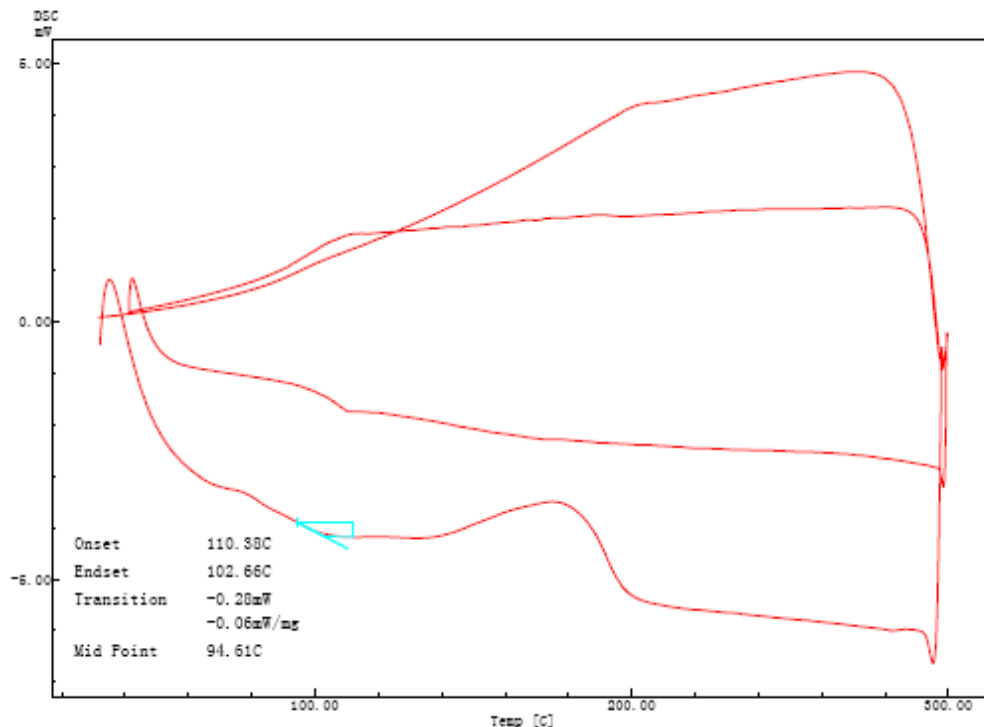


Figure S11. The DSC curve of aPS obtained by cluster **1c**.

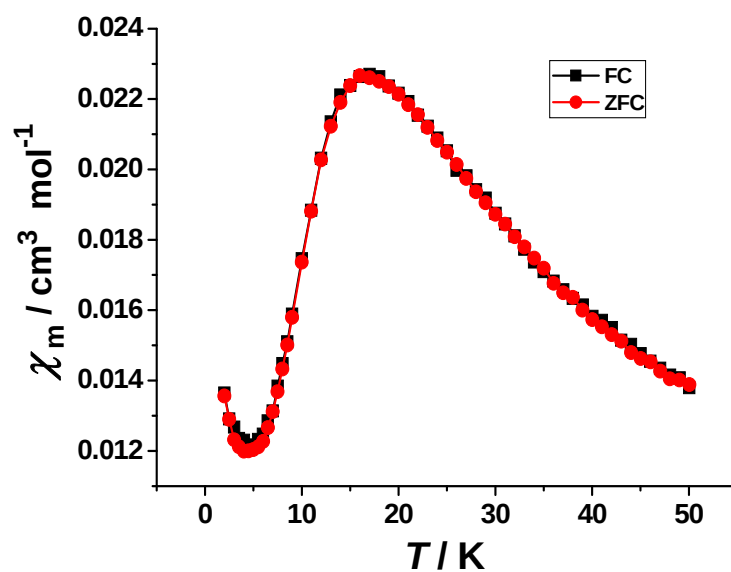


Figure S12. Plots of field-cooled (FC) magnetization (black square) and zero-field-cooled (ZFC) magnetization (red circle) at 20 Oe for **1**.

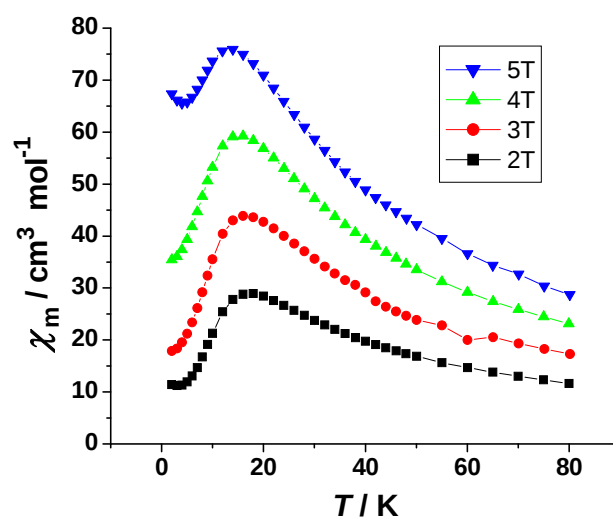


Figure S13. Plot of temperature dependence of χ_M versus T measured at different external fields of 2T (black square), 3T (red circle), 4T (green triangle) and 5T (blue reversed triangle) for **1**.

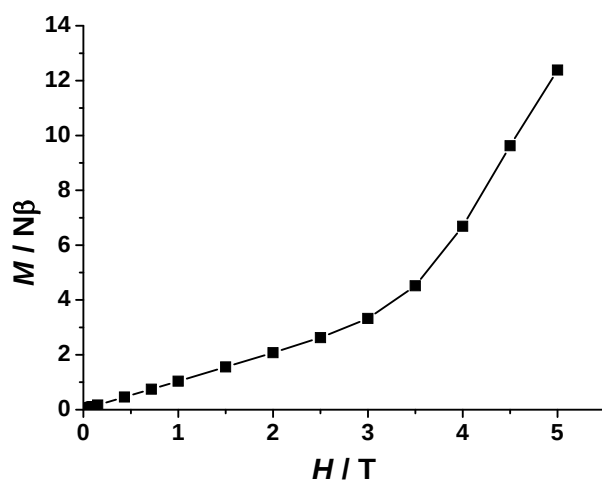


Figure S14. Plot of the field dependence of magnetization for **1** at 2 K.

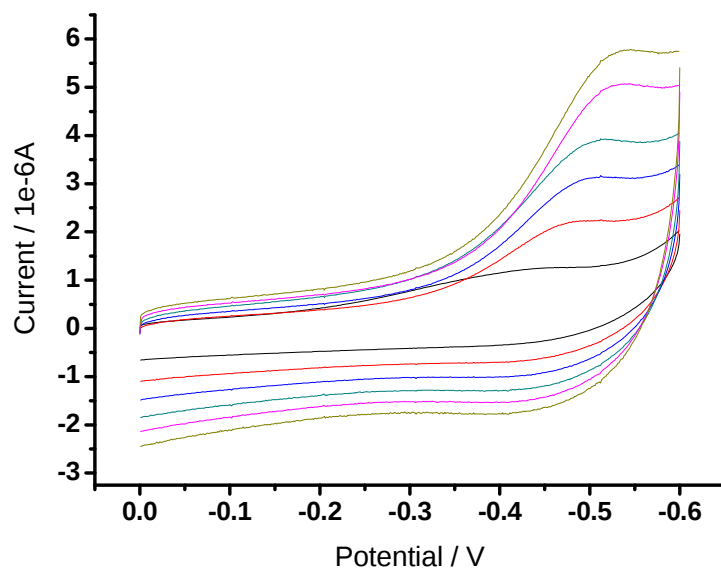


Figure 15. CV spectrum of **1** on gold electrode in acetonitrile and tetrabutyl ammonium bromide (1 mol / L) at different scan rates (from inner to outer: 100, 200, 300, 400, 500 and 600 mV^{-1}).