Electronic Supplementary Data

Convenient synthesis and Raman spectral characterization of diammonium monomolybdate(VI)

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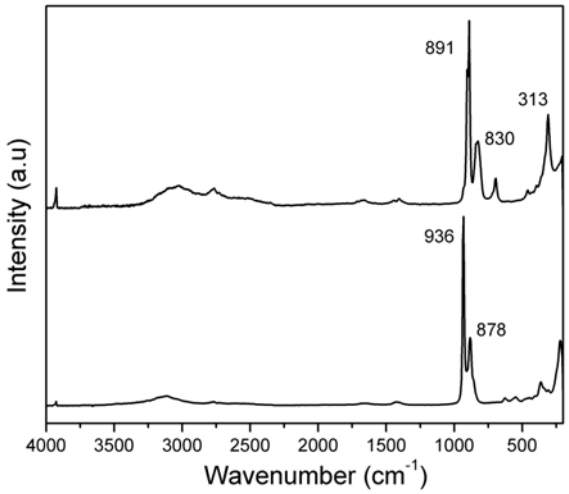

Fig. S1 — Raman spectra of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (**bottom**) and $(NH_4)_2MoO_4$ **1** (**top**). (υ_1= 891; υ_2 & υ_4= 313; υ_3= 830)

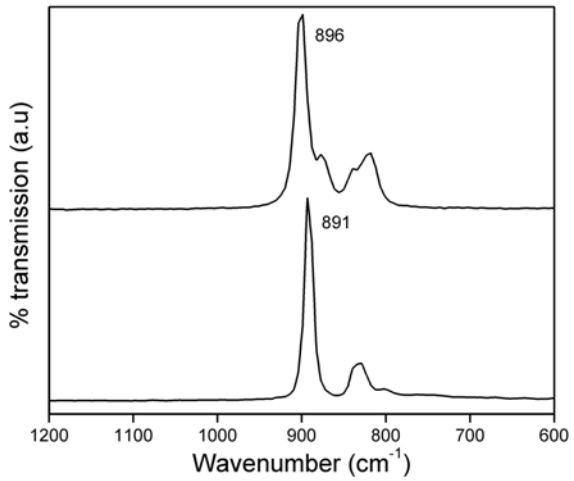

Fig. S2 — Raman spectra of solid (**bottom**) and aqueous solution (**top**) of $Na_2MoO_4\cdot 2H_2O$

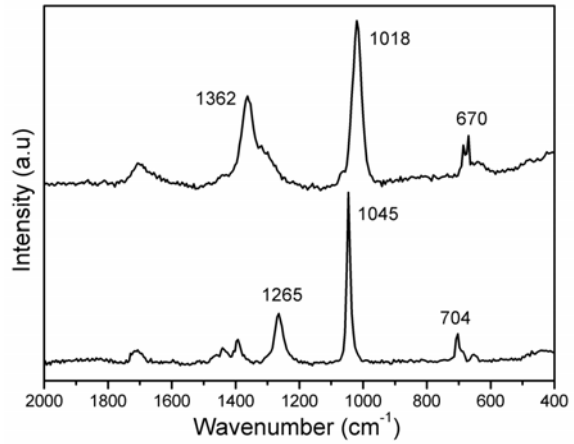

Fig. S3 — Raman spectra of solid $(NH_4)HCO_3$ (**bottom**) and aqueous solution of $(NH_4)HCO_3$ (**top**)

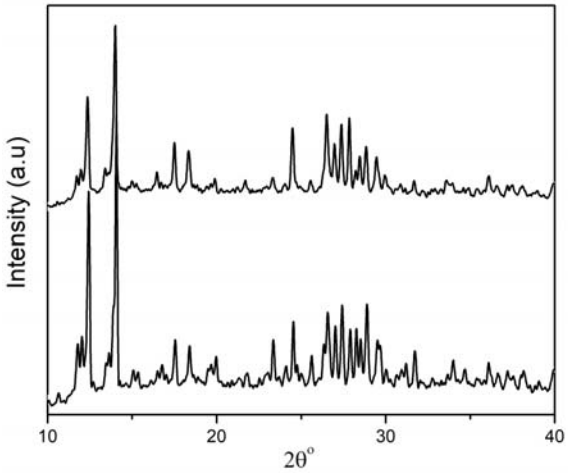

Fig. S4 — X —ray powder pattern of Sigma Aldrich sample $(NH_4)_2MoO_4$ (**bottom**) and $(NH_4)_2MoO_4$ **1** (**top**)

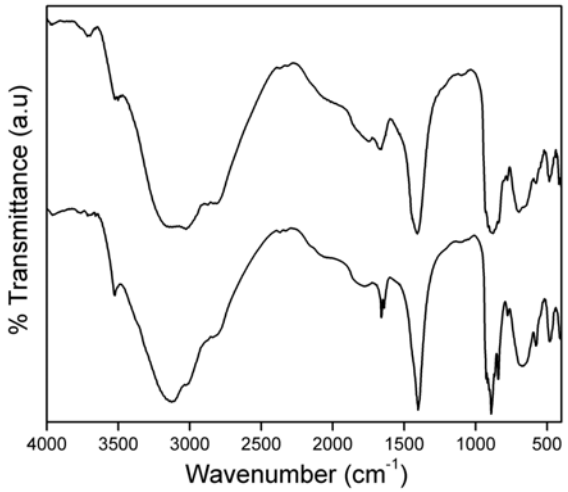

Fig. S5 — IR spectra of Sigma Aldrich sample $(NH_4)_2MoO_4$ (**bottom**) and $(NH_4)_2MoO_4$ **1** (**top**)

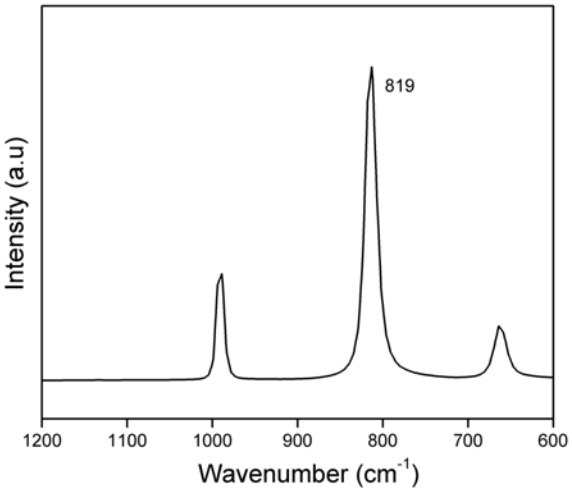

Fig. S6 — Raman spectrum of MoO_3 obtained by pyrolysis of $(NH_4)_2MoO_4$ **1** at 600 ^oC.

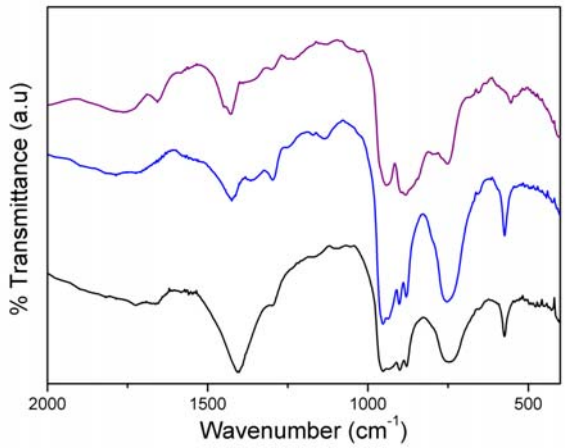

Fig. S7 — IR spectra of commercial $(NH_4)_2Cr_2O_7$ (**bottom**) and $(NH_4)_2Cr_2O_7$ obtained from ammoniacal solution of CrO_3 (**middle**) and $(NH_4)_2CrO_4$ (**top**) obtained by mechanothermal synthesis.

Mechanothermal synthesis of $(NH_4)_2CrO_4$

Ammonium dichromate (1.26 g, 5 mmol) was taken in a mortar and pestle and mixed with ammonium bicarbonate (0.79 g, 10 mmol). The mixture was thoroughly ground for 10 minutes to obtain fine yellow powder. The Raman spectrum of the powder indicated formation of tetrahedral species. The powder was taken in a glass beaker and kept in a laboratory oven preheated to 90 ^{o}C. After ~10 minutes, the reaction vessel was removed from the oven and kept in a desiccator to attain room temperature. Yield 95 %. The IR spectrum of the product is displayed in Fig. S7.
IR (cm^{-1}) — 3593 —2279 (broad), 1432, 936, 884, 753, 548; Raman — 872, 838, 376, 337.

Reaction of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ with $(NH_4)HCO_3$

Ammonium paratungstate (1.5 g, 0.5 mmol) was taken in a mortar and pestle and mixed with an excess of ammonium bicarbonate. The mixture was thoroughly ground for 30 minutes to obtain a fine powder. A Raman spectral study of the powder did not show any new band for the formation of a tetrahedral W species. Unlike Mo and Cr, this reaction did not afford any new W product other than the starting material viz. $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$.

$$(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O \xrightarrow[\text{ii) 90 °C}]{\text{i) Grind with excess } (NH_4)HCO_3} (NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$$

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