Facile Synthesis of Silver Nano/Micro- Ribbons or Saws assisted by Polyoxomolybdate as Mediator Agent and Vanadium (IV) as reducing agent.

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Experimental Section :

Sample preparations

{VOPMo$_{12}$}-{AgOac}- The vanadyl (IV) salt $H(V^{IV}O)[PMo_{12}O_{40}]$ has been synthesized following previous published procedure.[1] Silver acetate (183 mg, 1.1 mmol) was added to a light green acetonitrile solution (20 mL) of $H(V^{IV}O)[PMo_{12}O_{40}]$ (500 mg, 0.2 mmol) and the resulting mixture was vigorously stirred for 30 min. A dark black precipitate was removed from the solution by filtration. After three days at room temperature, gleaming metallic 1D-nanostructures were observed in the orange solution. These 1D-structures were recovered by centrifugation and washed with acetonitrile.

{PMo$_{11}$V}-{AgOac}- The tetrabutylammonium salt of reduced undecamolybdo-vanadophosphate was synthesized following the synthesis of the ammonium salt previously described.[2] Ammonium was just replaced by tetrabutylammonium in the present synthesis procedure. A dark blue solution of $(TBA)_5PMo_{11}VO_{40}$ (500 mg, 0.17 mmol) in acetonitrile (20 mL) was heated at 70°C and vigorously stirred for 15 min after addition of silver acetate (183 mg, 1.1 mmol). A dark precipitate, containing POM and AgOac, was removed by filtration. The bright orange solution was allowed to stay at room temperature for three days. Silver wires were recovered by centrifugation and washed with acetonitrile.

{PMo$_{11}$V}-{AgCO$_3$}- The same previous procedure was used except that silver carbonate (100 mg, 0.725 mmol) was added instead of silver acetate.

{PMo$_9$}-{Vacac}-{AgOac}- $Na_3H_6PMo_9O_{34}$ was prepared according to previous published procedure.[3] An acetonitrile solution of vanadyl acetylacetonate (263 mg, 1 mmol, 20 mL) was heated at 70°C. $Na_3H_6PMo_9O_{34}$ (500 mg, 0.33 mmol) was then added. After 15 min, silver acetate (330 mg, 2 mmol) was added to the dark blue solution at 70°C. After 5 min, the green filtrate solution was kept at room temperature. Three days later, gleaming wires were visually observed in the orange solution.

{PMo$_9$}-{Vacac}-{AgOac}-. *Synthesis in the dark* - The same previous procedure was used but crystallization was realized in the dark. After three days, particles were observed in the orange solution.

{PMo$_9$}-{Vacac}-{AgOac}- *Synthesis at 4°C* - The same previous procedure was used but crystallization was realized at 4°C. No visible particle was observed after three months and only nanoparticles were detected by TEM.

{PMo$_9$}-{Vacac}-{AgOac}. *Excess of silver acetate*- The same previous procedure was used except for the amount of silver acetate added (495 mg, 3 mmol). Silver saws assembled in small balls are obtained after three days.

Sample characterizations

The scanning electronic microscopy (SEM) (JEOL JSM-5800LV microscope) equipped with EDX probe of Oxford Instrument; acceleration is 15 kV. Drops of acetonitrile suspension were dropped on a glass plate for evaporation of the solvent; particles were selected under binocular microscope before deposition on adhesive. Transmission electronic microscopy (TEM) (microscope JEOL 100 CX2) was performed by drying the drop of acetonitrile suspension deposited on a copper grid. Powder X-ray diffraction patterns (XRD) were recorded at room temperature with a Siemens D 5000 diffractometer using Cu K_{α} radiation (λ = 1.5418 Å).

1 H. An, Y. Li, D. Xiao, E. Wang and C. Sun, *Cryst. Growth Des.*, 2006, **6**, 1107.
2 C. Marchal-Roch, C. Julien, J. F. Moisan, N. Leclerc-Laronze, F. X. Liu and G. Herve, *Appl. Catal., A*, 2004, **278**, 123.
3 M. Leyrie, *C. R. Acad. Sci. Paris*, 1971, **273**, 569

Supplementary Figures Captions:

Fig. S1. a- SEM pictures of {$PMo_{11}V$}-{AgOac} and b- TEM picture of fibers of {$PMo_{11}V$}-{AgOac}. Arrow A shows the presence of silver nanoparticles; arrow B shows the superposition of silver nanoplates; arrow C shows nanowires of various length and width with very smooth surfaces.

Fig. S2. a- determination of the stoechiometry reaction between $[PMo_9O_{31}(OH_2)_3]^{3-}$ with $VO(acac)_2$ in CH_3CN follow by UV-visible spectroscopy. B- IR spectrum and TGA curve of $Na_3H_2TBA_4[PMo_9V_3O_{40}]$.

Fig. S3. 1D-microstructures of {PMo_9}-{Vacac}-{AgOac}, a- by SEM and b- corresponding EDX cartography centred on Mo atoms, c- Ag atoms and d- V atoms.

Fig. S4. SEM picture of {PMo_9}-{Vacac}-{AgOac} with higher concentration compared with Fig. S3..

Fig. S5. XRD powder of 1D-microstructure shown in fig S3, compared to fcc silver referenced N° CAS : 7440-22-4. Calculated parameter a = 4.08Å

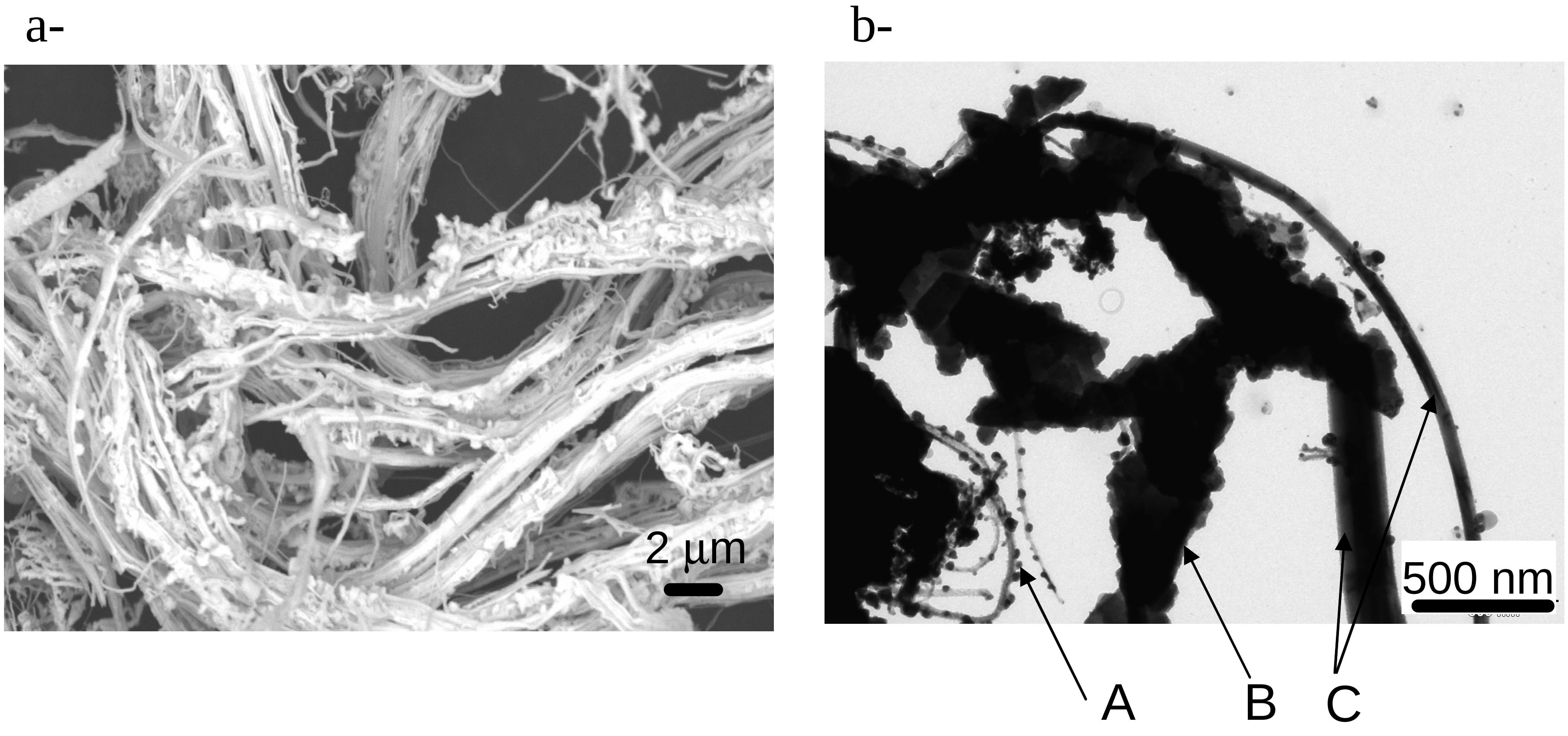
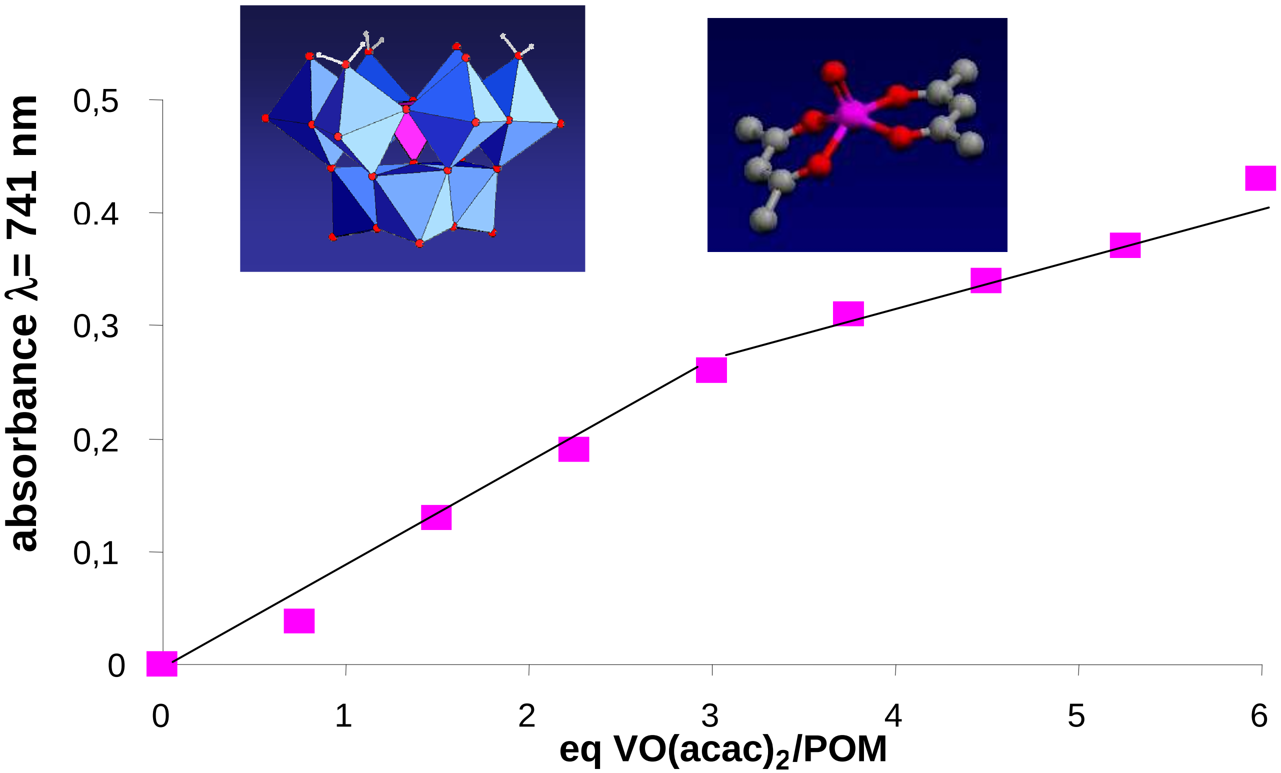


Figure S1

Reaction of $[PMo_9O_{31}(OH_2)_3]^{3-}$ with $VO(acac)_2$ in CH_3CN.



Stoechiometry : **3 vanadyl per $[PMo_9O_{31}(OH_2)_3]^{3-}$**

Figure S2a

Characterization of $Na_3H_2TBA_4[PMo_9V_3O_{40}]$

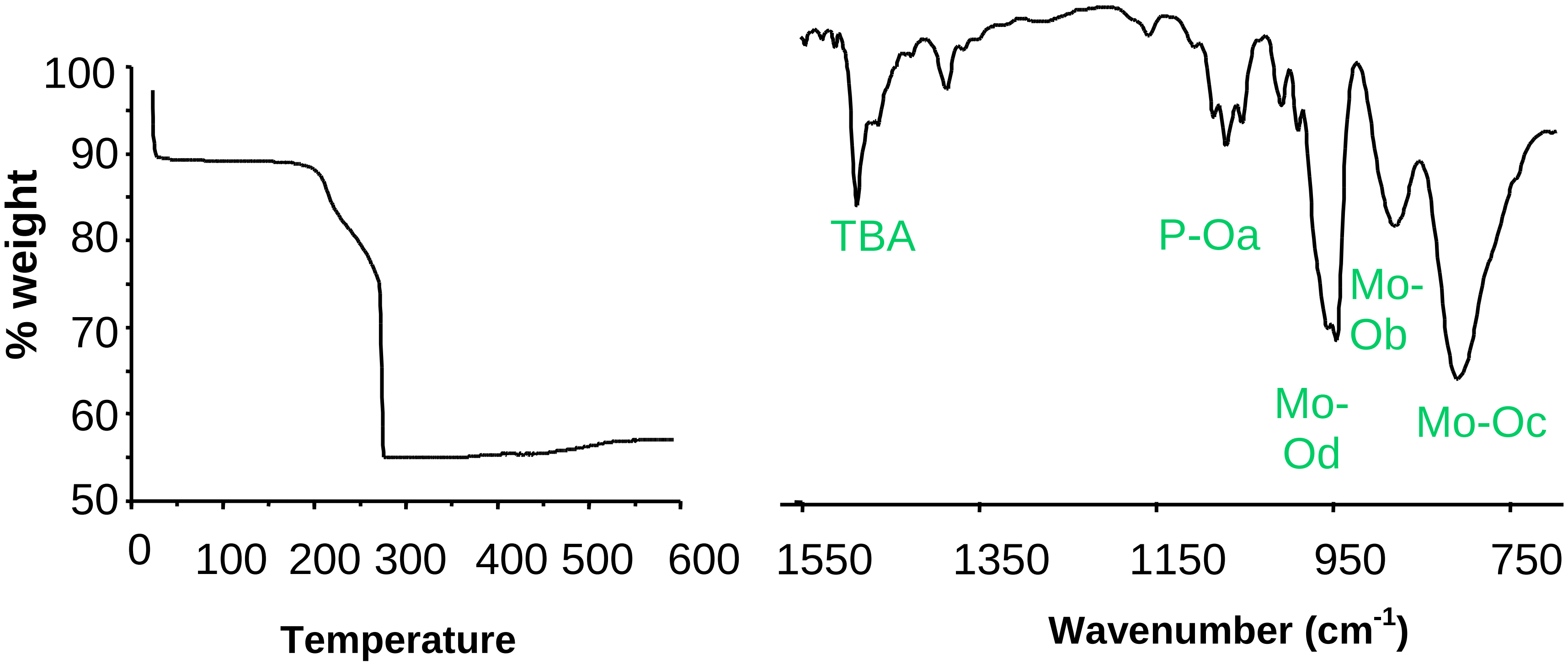


Figure S2b

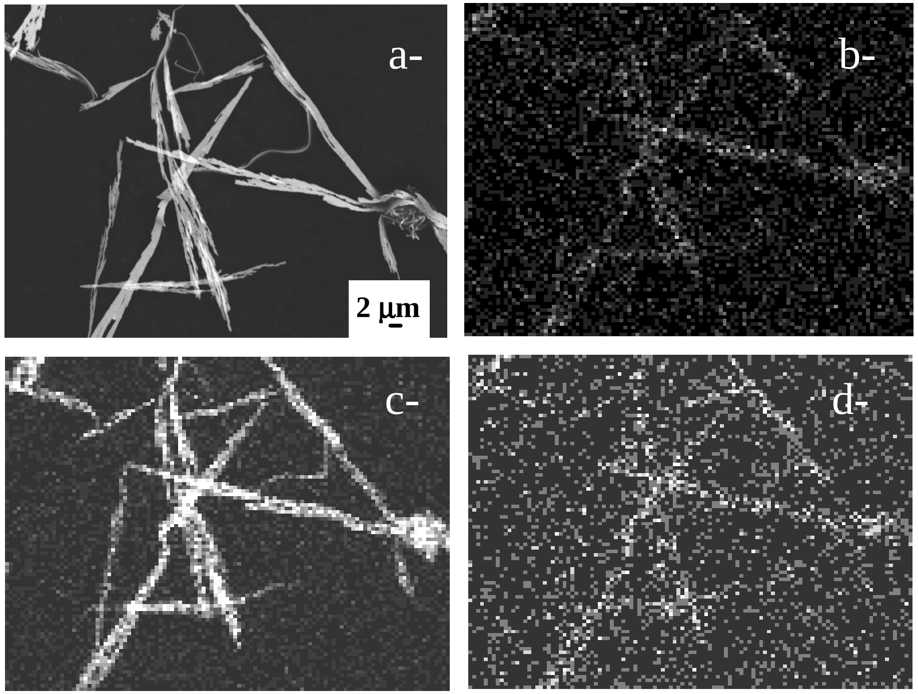


Figure S3

Figure S4

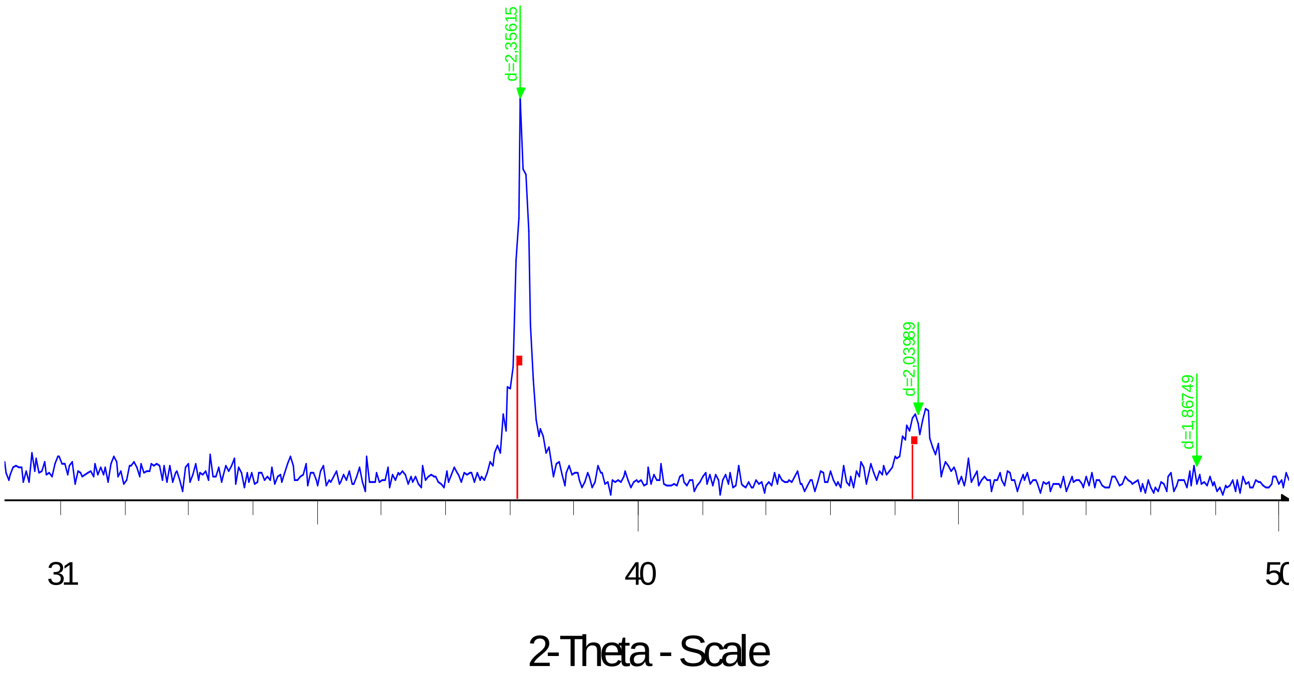


Figure S5