

Electronic Supplementary Information

Solid-State Transformation of Single Precursor Vanadium Complex Nanostructures to V_2O_5 and VO_2 : Catalytic Activity of V_2O_5 for Oxidative Coupling of 2-Naphthol

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1. Single crystal data collection and refinements of $[V_{10}O_{28}][(CH_3)_2NH_2]_6(H_2O)$

Single crystal X-ray diffraction data of the new compound is collected on a Bruker APEX SMART CCD system that uses graphite monochromated MoK α radiation ($\lambda=0.71073$ Å). The structure analysis is done using WinGXⁱ program embedded with SHELXS-97ⁱⁱ and refined by least square methods on F² using SHELXL-97 without any absorption corrections. Non-hydrogen atoms are refined anisotropically and hydrogen atoms on the C-atoms of dimethylammonium cations are fixed at the calculated positions and refined isotropically using a riding model. Hydrogen atoms on the N-atom of dimethylammonium cations are located in difference Fourier maps and refined isotropically. But the H-atoms on the water of crystallization could not be located. N-atom of a dimethylammonium cation is disordered and the H-atoms of the disordered dimethylammonium cation are not added. Information concerning X-ray data collection and structure refinement, bond lengths of the compound is summarized in Table S1. CCDC 945650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Crystal Structure of $[V_{10}O_{28}][(CH_3)_2NH_2]_6(H_2O)$

One of the single crystals obtained by slow evaporation of the $[(C_5H_5N)_2V_2O_3 \cdot H_2O]$ nanostructures from DMF (solvent) is identified to determine the structure in solid state by single crystal X-ray crystallography. X-ray diffraction analysis reveals that, the compound crystallizes in orthorhombic space group *Cmca*. The asymmetric unit contains one half of the decavanadate anion $(V_{10}O_{28})^{6-}$, two dimethylammonium cations, half of two dimethylammonium cations and one water molecule of crystallization. The crystal structure of the compound shows the presence of discrete decavanadate cluster along with water and dimethylamine (Figure S4a). All the dimethyl amines are protonated. Bond lengths and bond

angles of the decavanadate cluster anions are comparable to those found in the literature.ⁱⁱⁱ In the $V_{10}O_{28}^{6-}$, each vanadium ion is in distorted octahedral coordination environment and coordinated with six oxo oxygens (terminal & bridging oxygen). The decavanadate cluster anions are interconnected through intermolecular hydrogen bonding interactions via dimethylammonium cations. Due to the presence of hydrogen bond donor as well as acceptor sites, the molecule shows intermolecular hydrogen bonding interactions (Figure S4b). In the polymeric network, hydrogen on N1 atom shows intermolecular hydrogen bonding interactions with three μ_2 -oxygens (O3 & O5), hydrogen on N2 and N4 atoms show interaction with μ_2 -oxygens O8, O15 and O11 respectively. The H-atom on N4 also shows interaction with terminal oxygens (O17 & O18) and μ_2 -oxygen (O2). Thus H-atoms of dimethylammonium cations connect two $V_{10}O_{28}^{6-}$ units and the H-atom on N3 of dimethylammonium cations connects three $V_{10}O_{28}^{6-}$ units. Thus dimethylammonium cations act as H-bonded bridge among the decavanadate cluster anions and in solid state it forms a 3D supramolecular architecture (Figure S4c)

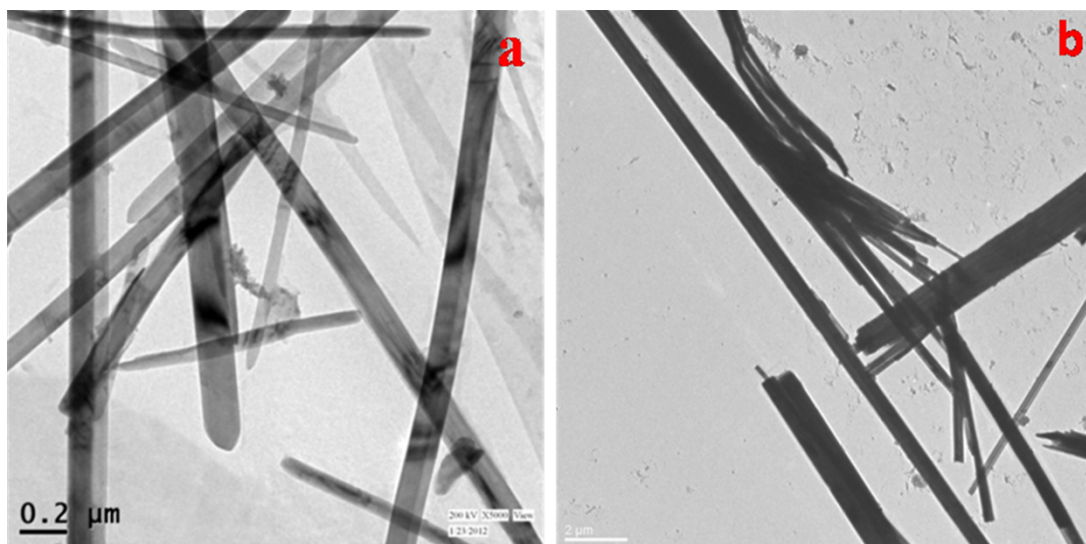


Figure S1: TEM images of the (a) synthesized V₂O₅ nanowire (b) V₂O₅ nanowire after catalysis.

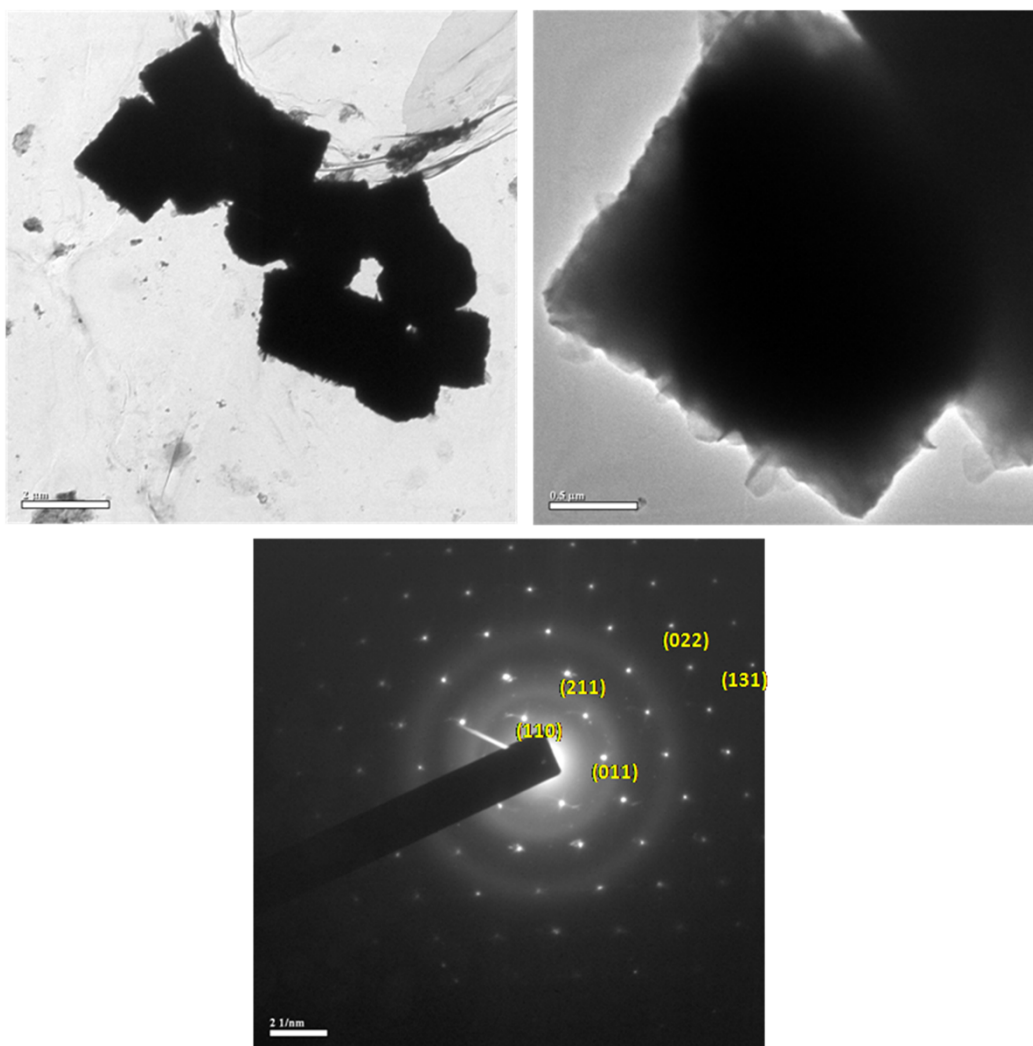


Figure S2: TEM and SAED pattern of the synthesized VO₂ octahedra.

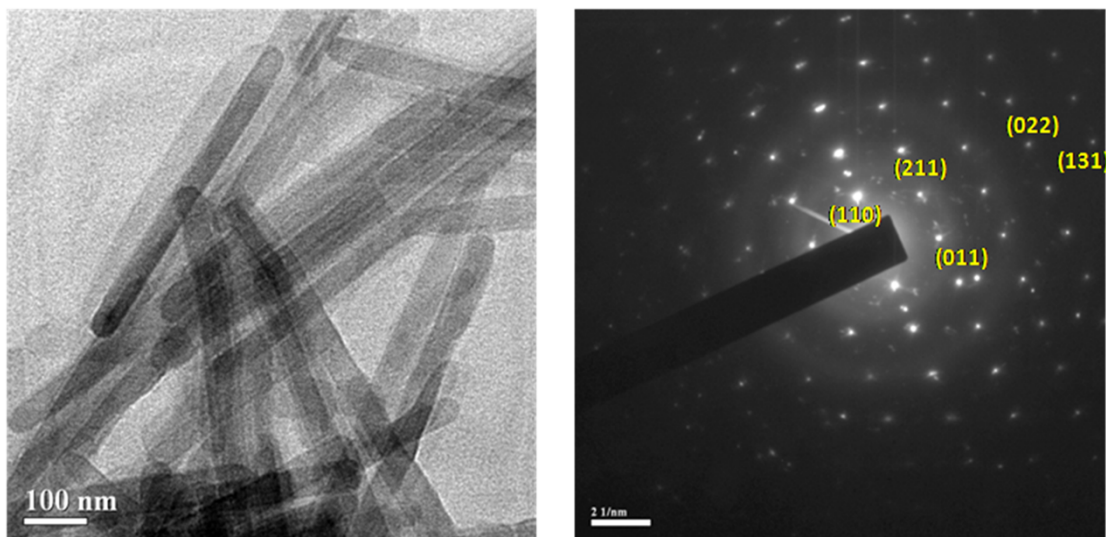


Figure S3: TEM and SAED pattern of the synthesized VO₂ nanowire.

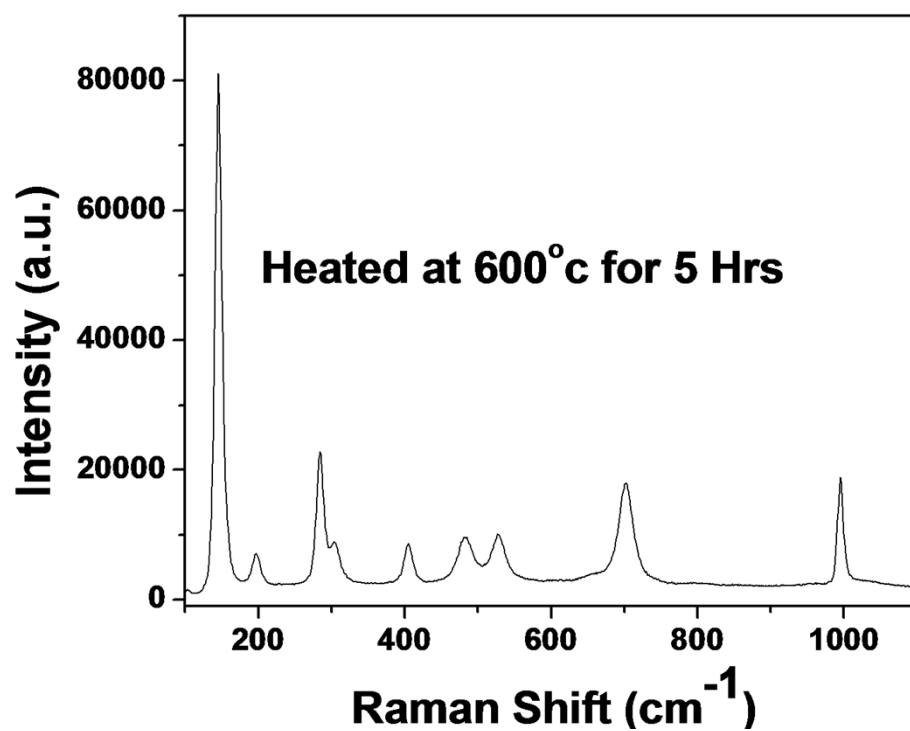


Figure S4: Raman spectrum of V_2O_5 obtained after calcination of green $[(C_5H_5N)_2V_2O_3 \cdot H_2O]$ at 600°C.

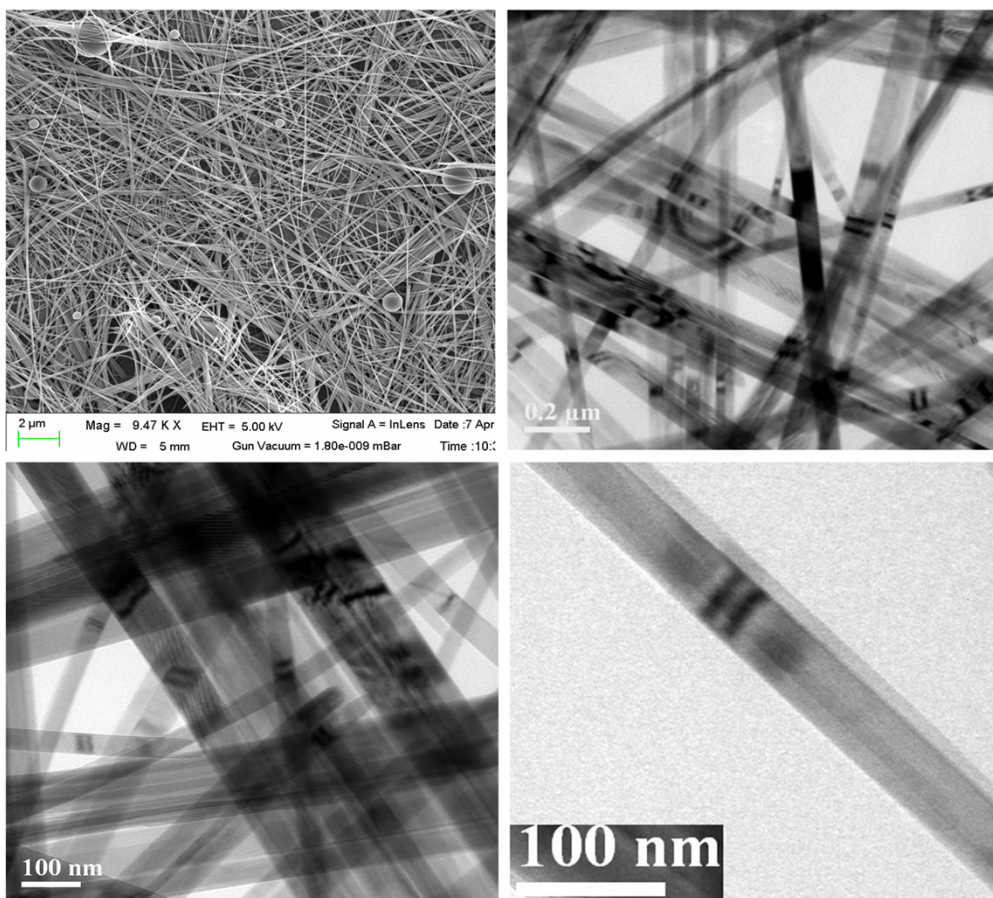


Figure S5: FESEM and TEM images of synthesized $[(\text{C}_5\text{H}_5\text{N})_2\text{V}_2\text{O}_3 \cdot \text{H}_2\text{O}]$ nanobelt.

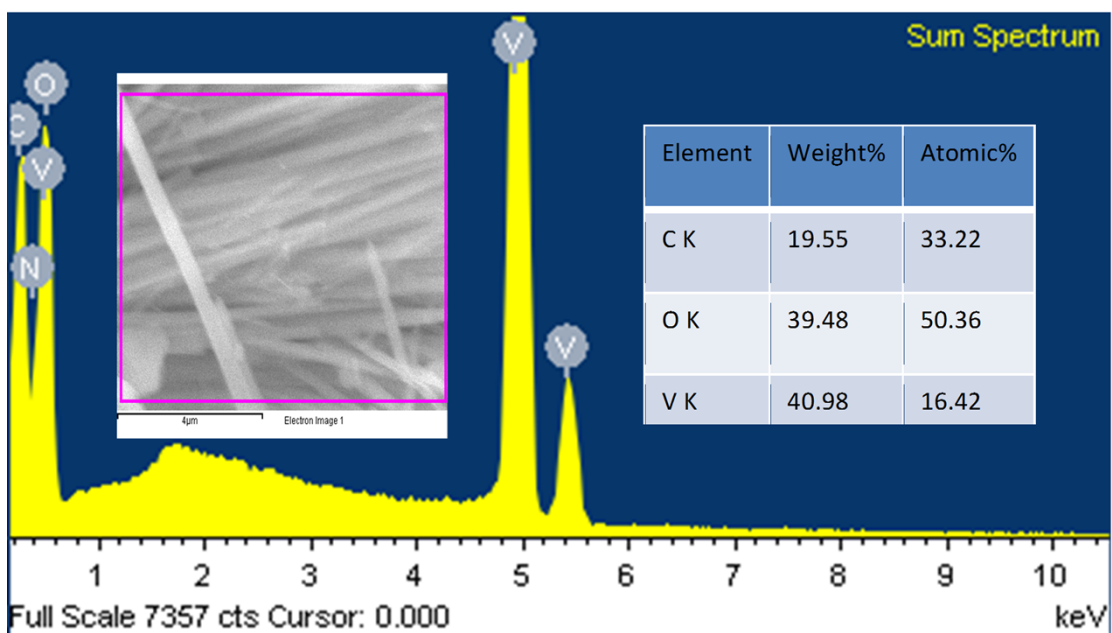


Figure S6: EDX spectrum of synthesized $[(C_5H_5N)_2V_2O_3.H_2O]$ nanobelt.

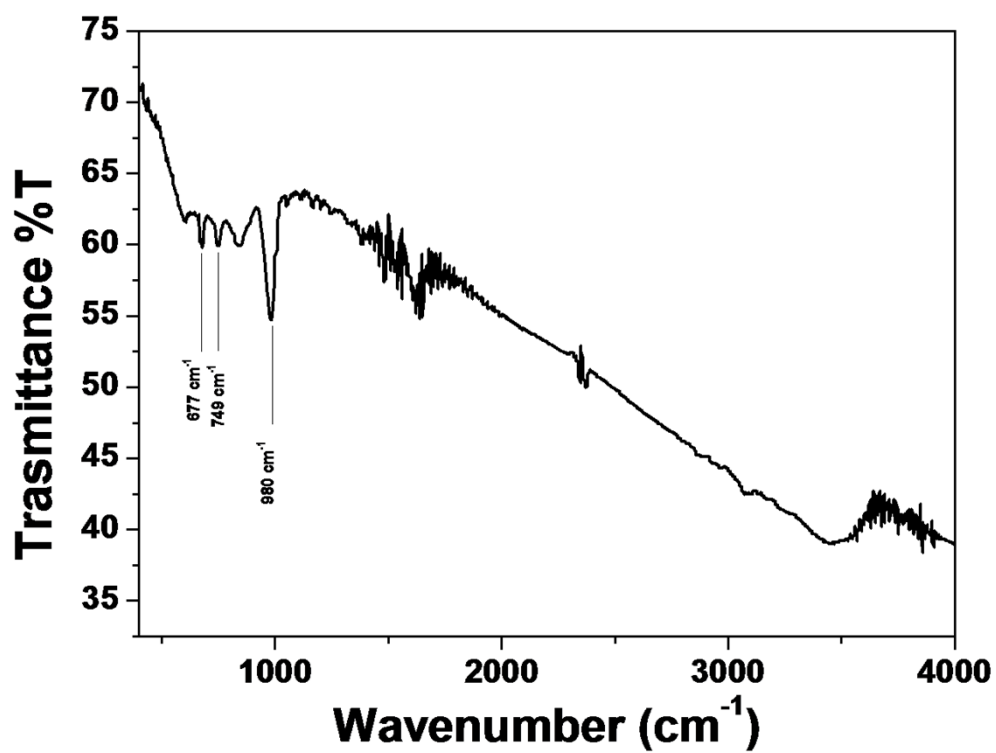


Figure S7: FTIR spectrum of synthesized [(C₅H₅N)₂V₂O₃.H₂O] nanobelt.

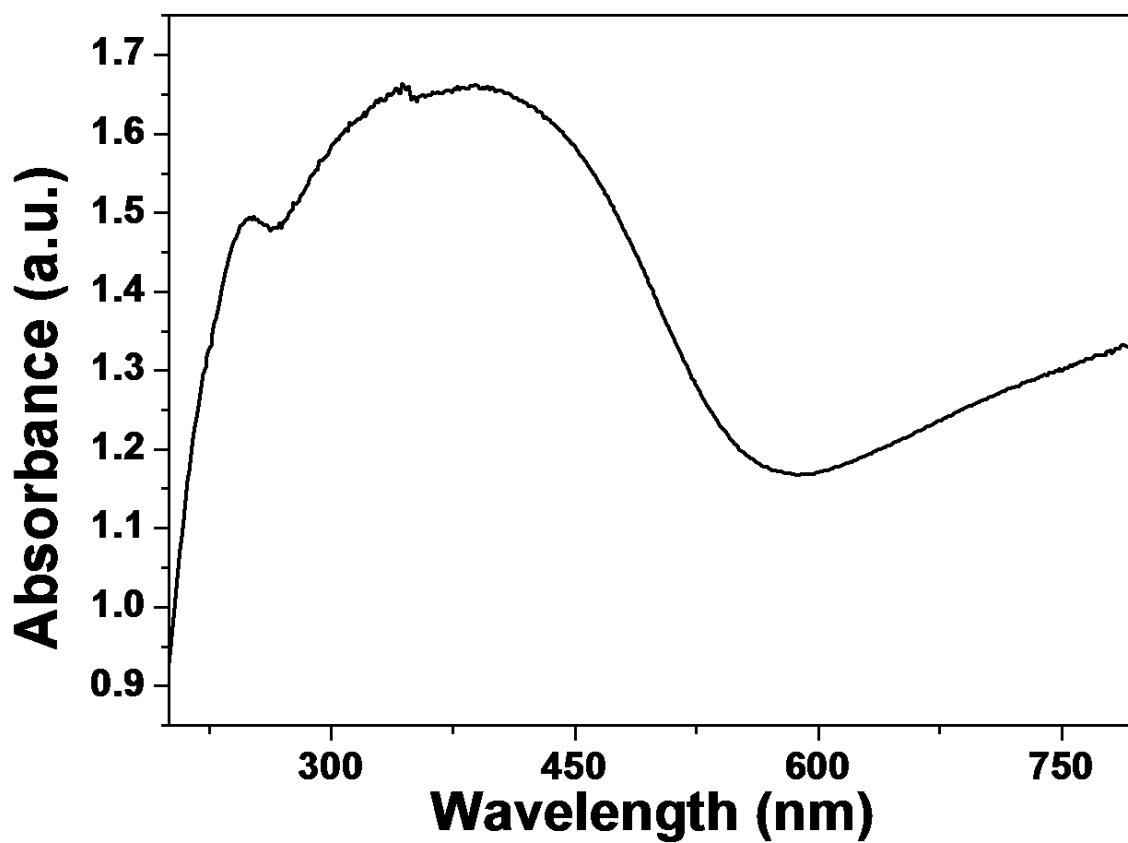


Figure S8: DRS spectrum of synthesized $[(C_5H_5N)_2V_2O_3.H_2O]$ nanobelt.

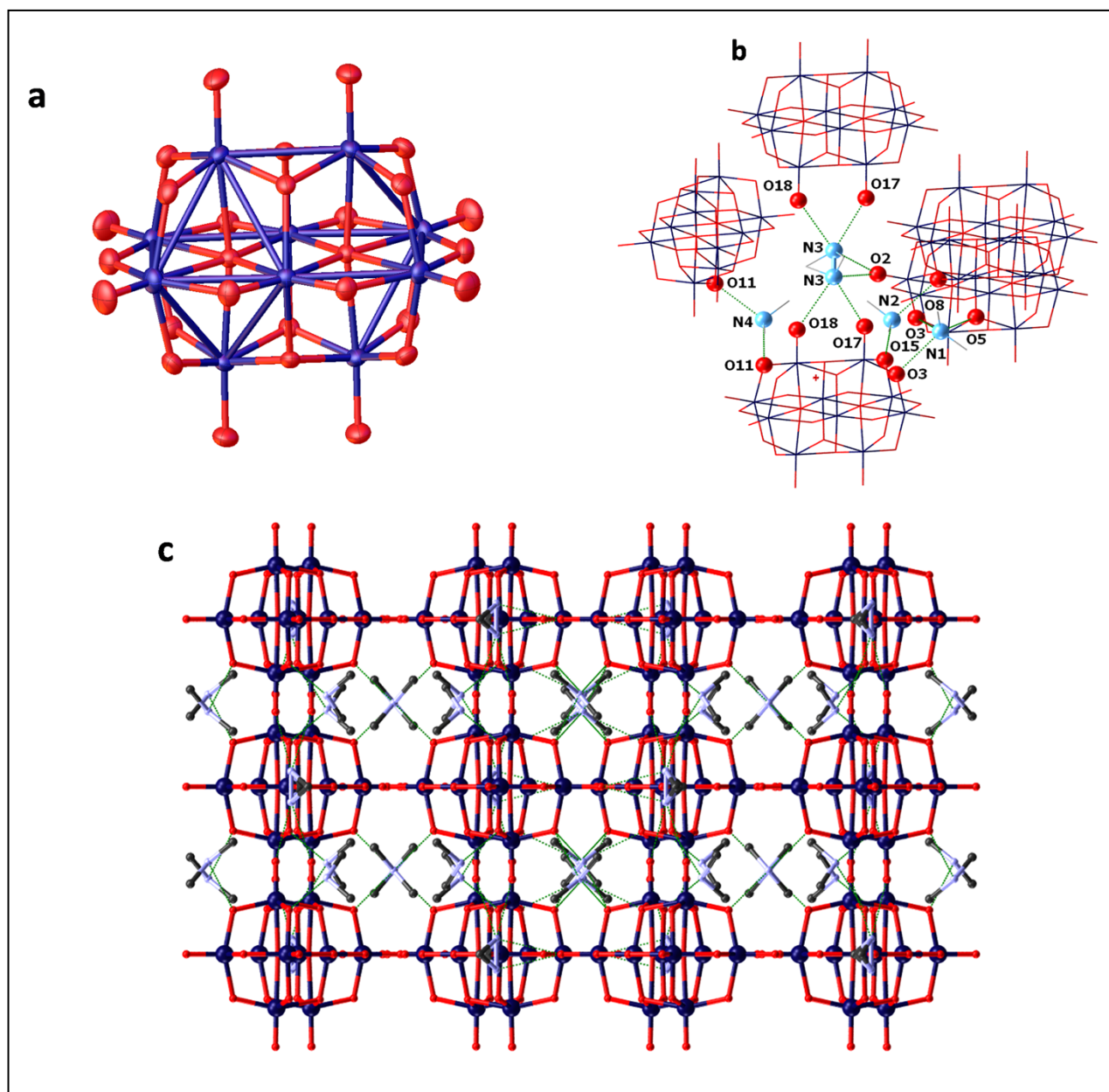
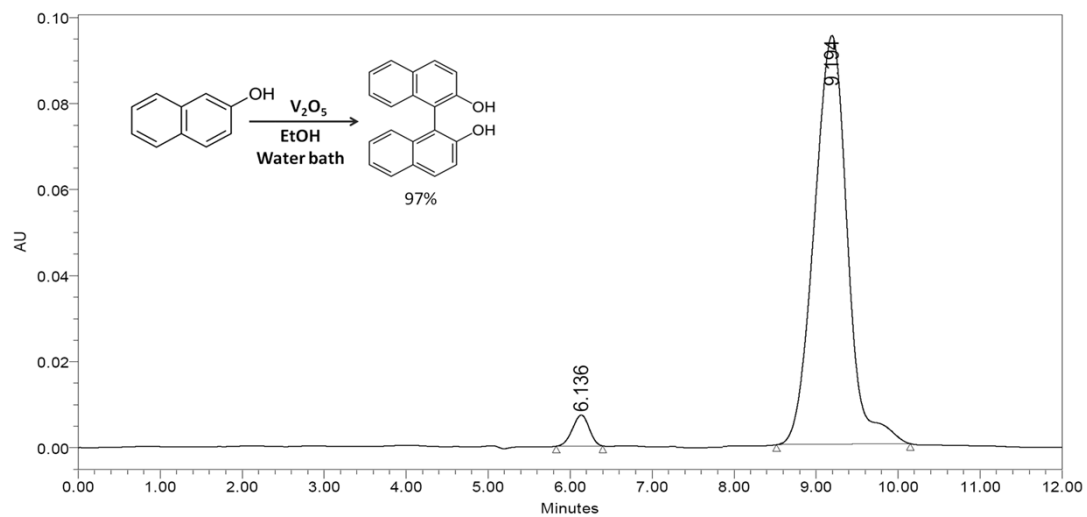


Figure S9: (a) Ortep view of $V_{10}O_{28}^{6-}$ unit (b) Ball and stick model showing H-bonded network of the compound in solid state. (c) View of the 3D H-bonded network along the crystallographic b axis. Colour code: V: deep blue; O: red; N: light blue; C: black; H-bonding interactions green dotted line. Hydrogen atoms are not shown for clarity.

Table S1. Crystallographic Data for the compound

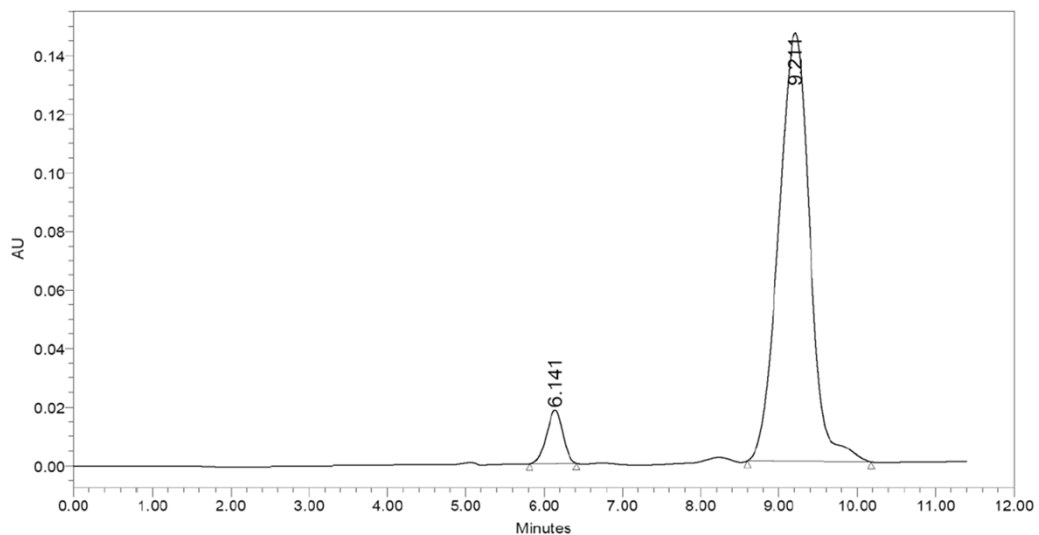
Empirical formula	C ₁₂ H ₅₀ N ₆ O ₂₉ V ₁₀
Formula weight	1251.97
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Cmca
Unit cell dimensions	a = 13.867(3) Å b = 18.913(4) Å c = 30.893(7) Å
Volume	8102(3) Å ³
Z	8
Density (calculated)	2.08 Mg/m ³
Absorption coefficient	2.32 mm ⁻¹
F(000)	4928.0
Crystal size (mm)	0.20 x 0.10 x 0.10
Theta range for data collection	1.94 to 26.32°.
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 23, -36 ≤ l ≤ 38
Reflections collected	50579
Independent reflections	4276 [R(int) = 0.1100]
Completeness to theta = 26.32°	99.3 %

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4303 / 0 / 314
Goodness-of-fit on F ²	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.0956
R indices (all data)	R1 = 0.0881, wR2 = 0.1150
Largest diff. peak and hole	1.483 and -0.396 e.Å ⁻³



	RT	Area	% Area	Height
1	6.136	102489	3.71	7226
2	9.194	2657704	96.29	95084

Figure S10: Shows the HPLC diagram of product mixture after V_2O_5 catalysed oxidative coupling of β -naphthol.



	RT	Area	% Area	Height
1	6.141	450672	10.06	18105
2	9.211	4029172	89.94	146320

Figure S11: Shows the HPLC diagram of product mixture after oxidative coupling of β -naphthol catalysed by V_2O_5 nanopowder from Merck.

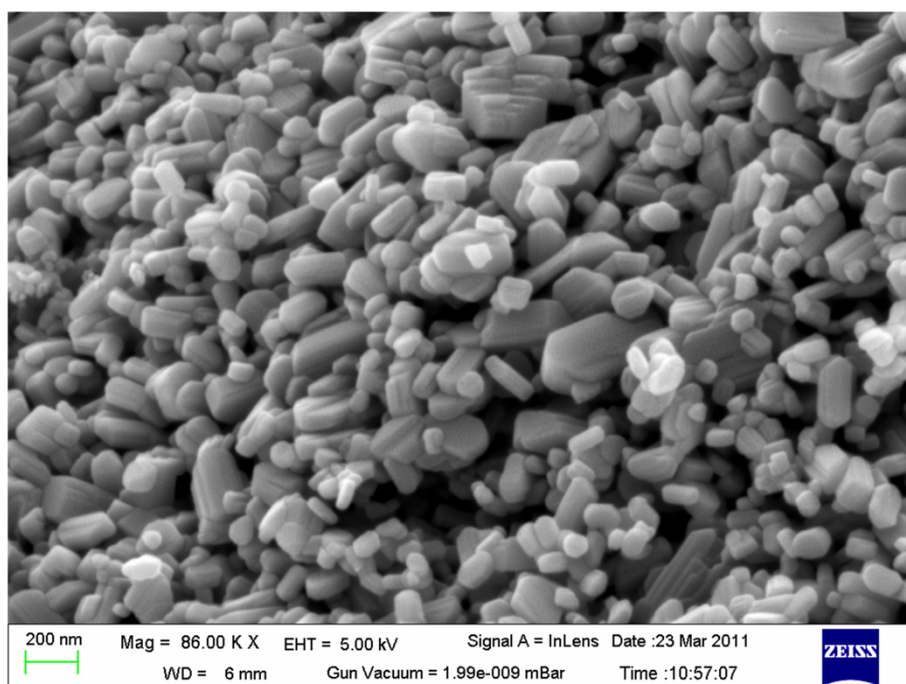


Figure S12: SEM image of the as obtain V₂O₅ nanopowder from Merck.

References

- i. L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.
- ii. G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112.
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