Supporting Information for

Inorganic-Organic Hybrid Polyoxovanadates Based on [V$_4$O$_{12}$]$^{4-}$ or [VO$_3$]$_2^{2-}$ Clusters: Controllable Synthesis, Crystal Structures and Catalytic Properties in Selective Oxidation of Sulfides

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Figure S4. The FT-IR spectra of complex 3.

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Table S1. Bond valence sum calculations for complexes 1-3.[a][1-3]

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<th>V3</th>
<th>V4</th>
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[a] The calculations were performed twice for each individual vanadium atom using bond-valence parameters presented by Brese and O’Keeffe. The oxidation state of atom i is given by \( \sum v_j = \gamma V \) with \( v_j = \exp(-R_j d_{ij}/b) \). Here b is taken to be a ‘universal’ constant equal to 0.37 Å, \( v_j \) is the valence of a bond between two atoms i and j, \( R_j \) is the empirical parameter, and \( d_{ij} \) is the observed bond length.

Table S2. Selected Bond lengths [Å] and angles [°] for complexes 1-3.

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Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+2,-y+1,-z; #4 -x+1,-y+2,-z.

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Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+2,-y,-z+1; #3 -x+1,-y+2,-z; #4 -x+1,-y+1,-z.

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Symmetry transformations used to generate equivalent atoms: #1 -x,y+1/2,-z+1/2; #2 -x,-y+1,-z+1; #3 -x+1,-y+2,-z; #4 -x+1,-y+1,-z; #5 -x+1,-y+1,-z+1.
Figure S1. The [Co₂O₂] square plane structure unit in complex 3.

Figure S2. The FT-IR spectra of complex 1.

Figure S3. The FT-IR spectra of complex 2.
Figure S4. The FT-IR spectra of complex 3.

Figure S5. The FT-IR spectra of complex 1 after each catalytic cycle.

Figure S6. The simulated, experimental and after three catalytic cycles PXRD patterns of complex 1. Simulation based on the SXRD data.
Figure S7. The simulated (black) and experimental (red) PXRD patterns of complex 2. Simulation based on the SXRD data.

![PXRD pattern of complex 2](image)

Figure S8. The simulated (black) and experimental (red) PXRD patterns of complex 3. Simulation based on the SXRD data.

![PXRD pattern of complex 3](image)


The detection limit of the inductively coupled plasma spectrometer (ICP-AES) on a SPECTRO ARCOS EOP analyzer is 0.002mg/L.

Figure S10. The crystal structure of Ni(1-vIM)$_4$Cl$_2$ (CCDC No. 1881006).
Figure S11. The crystal structure of complex \([\text{Co}_4(1-\text{vIM})_{14}]\text{[V}_4\text{O}_{12}]_2\cdot 6\text{H}_2\text{O}(4)\) (CCDC No. 1887006). a) Asymmetrical structural unit; b) Molecular structure.

S12. The crystallographic data of complex \([\text{Co}_4(1-\text{vIM})_{14}]\text{[V}_4\text{O}_{12}]_2\cdot 6\text{H}_2\text{O}(4)\).

Formula: C\(_{70}\)H\(_{95}\)N\(_{28}\)O\(_{30}\)Co\(_4\)V\(_8\); \(M_r=2451.97\); Crystal system: Triclinic; Space group: \(P\)-\(T\); \(a=12.76(3)\) Å, \(b=15.37(3)\) Å, \(c=16.00(3)\) Å; \(\alpha=68.37(3)\), \(\beta=66.71(3)\), \(\gamma=73.74(3)\); \(V=2644(9)\) Å\(^3\); \(Z=1\); \(\rho=1.540\) g cm\(^{-3}\); \(T=298(2)\) K; \(R_1=0.0874\); \(wR_2=0.1651\); \(GOF(F^2)=0.820\). More crystallographic data please check the Cambridge Crystallographic Data Centre (CCDC) with entry 1887006.

Reference: