Peptide functionalization of hybrid polyoxometalates

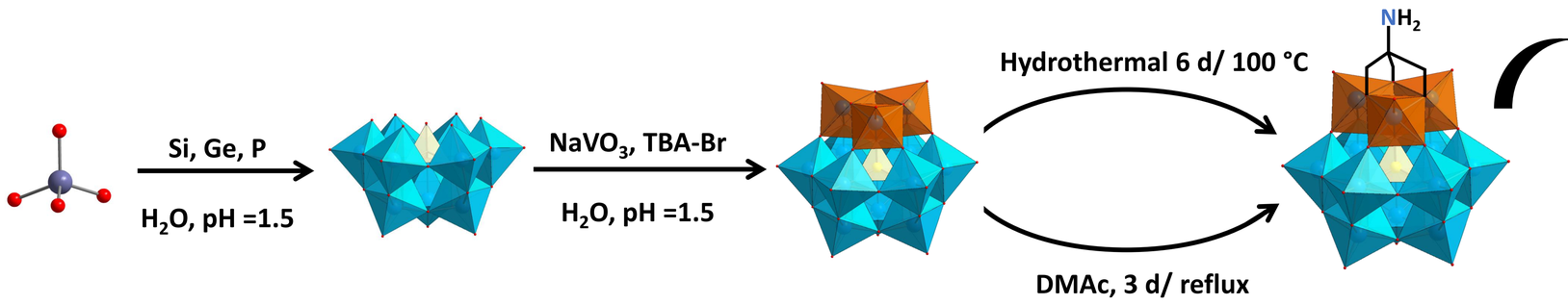
Teresa Bell[1,2,3] Nadiia Gumerova[1] Annette Rompel[1,2]

1) Universität Wien, Fakultät für Chemie, Institut für Biophysikalische Chemie, Josef-Holaubek-Platz 2, 1090 Wien, Austria; https://www.bpc.univie.ac.at,
2) Universität Wien, Fakultät für Chemie, Vienna Doctoral School in Chemistry (DoSChem), Währingerstraße 42, 1090 Wien, Austria,
3) https://doi.org/10.17952/38EPS.2026.P032

Introduction

Polyoxometalates (POMs) are discrete, water soluble, predominantly anionic polynuclear metal-oxo coordination compounds. They are constructed of an ionic core comprising corner- and edge-sharing pseudo-octahedral $\{MO_6\}$ units with early transition metals from group V or VI (M = $V^{IV/V}$, $Mo^{V/VI}$, $W^{V/VI}$).[1] The modification to organic-inorganic hybrid-POMs represents a growing area of interest. Organic molecules can be attached through ionic interactions (Class I) or bound covalently/ iono-covalently (Class II) to the inorganic core.[2] The combination of inorganic and organic physical properties can enhance the bioactivity and biospecificity[3], improve the stability[2], and expand the potential applications in biomedicine[4].
Hereby we concentrate on the synthesis of the hybrid POMs with amino- and carboxy-functions based on the two archetypes **Keggin** ($[XM_{12}O_{40}]^{n-}$), and **Wells-Dawson** ($[X_2M_{18}O_{62}]^{n-}$), where X = Al, Ge, SI, P; M = Mo, W, V; n = 3, 6.[5]

Keggin



^{51}V NMR: δ = -565 ppm.

^{51}V NMR: δ = -559 ppm.

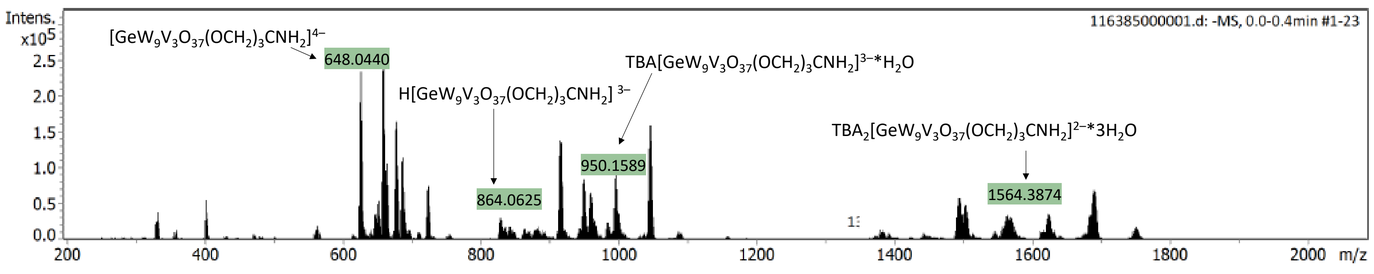
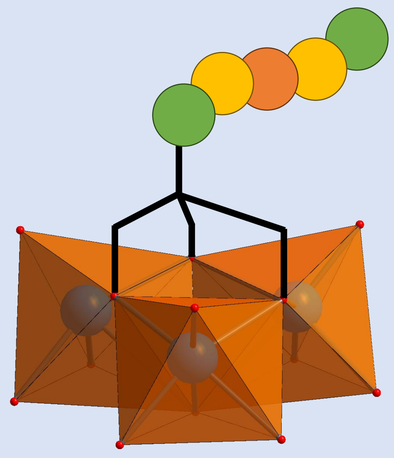


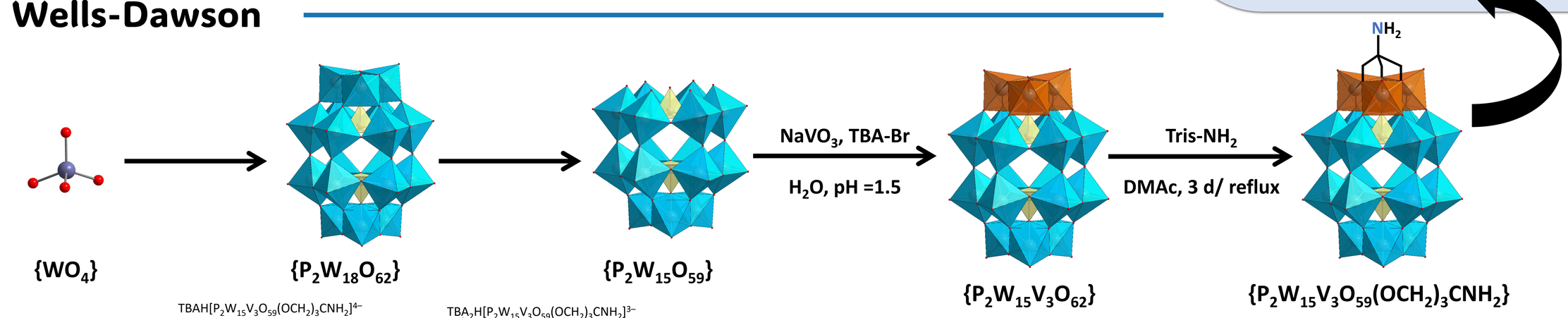
Fig.1 ESI-MS spectra of **$[GeW_9V_3O_{37}(OCH_2)_3CNH_2]^{4-}$**. Color code: blue – W, orange – V, yellow – P/Si/Ge.

The heteropolyanionic mixed-metal W/V POMs with different hetero atoms (Ge, Si, P) are synthesized by a step-by-step procedure from simple $[WO_4]^{2-}$ building blocks in an acidified aqueous solution through self-assembly in condensation reaction.[6][7]
The organic functionalization can be achieved through reaction under argon atmosphere and in the dark or through hydrothermal reaction (thermodynamic favored pathway).[8]
The Keggin and Wells-Dawson structures were analyzed with ^{1}H, ^{31}P, and ^{51}V nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR) and Electrospray Ionization Mass Spectrometry (ESI-MS).[9]



The advantages of hybrid POMs over traditional POMs lies in their enhanced functional properties, which result from combining POM attributes (e. g. redox capabilities) with organic framework characteristics, (e. g. high surface area, organized structure). The organic component of the hybrid POMs can be subjected to chemical modification either through pre-functionalization or post-functionalization.[2]
Therefore hybrid POMs can be used as "inorganic" amino acids in peptide synthesis.[4]

Wells-Dawson



^{51}V NMR: δ = -551 ppm.

^{31}P NMR: δ = -7.7 ppm, -13.6 ppm.

^{51}V NMR: δ = -599 ppm.

^{31}P NMR: δ = -7.8 ppm, -13.2 ppm.

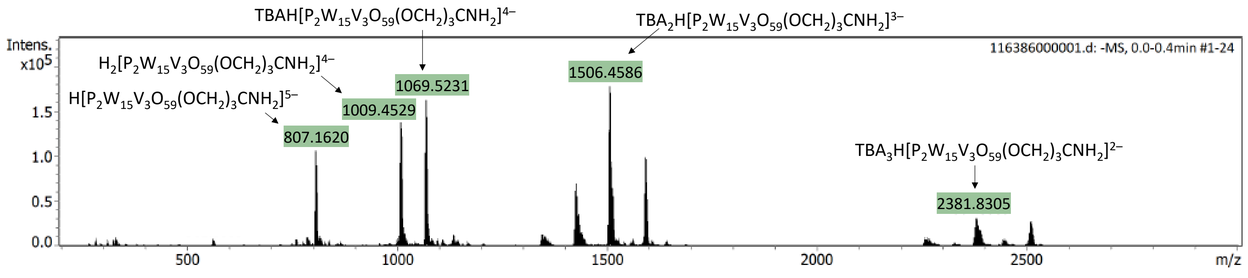
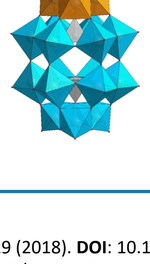


Fig.1 ESI-MS spectra of $[P_2W_{15}V_3O_{59}(OCH_2)_3CNH_2]^{6-}$.
with **TBA**: tetrabutylammonium $[N(C_4H_9)_4]^+$ and **TRIS**: tris-hydroxymethyl)aminomethane $-[(OCH_2)_3CNH_2]$. Color code: blue – W, orange – V, yellow – P.

Conclusion & Outlook

- Successful synthesis and characterization of Wells-Dawson type **$[P_2V_3W_{15}O_{59}(OCH_2)_3CNH_2]^{6-}$.**



- Successful synthesis and characterization of Keggin type **$[GeW_9V_3O_{37}(OCH_2)_3CNH_2]^{4-}$** and **$[SiW_9V_3O_{37}(OCH_2)_3CNH_2]^{4-}$.**



- Side-chain functionalization of amino acids with TRIS-functionalized Hybrid-POMs.

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teresa.bell@univie.ac.at
LinkedIn\Teresa Bell

annette.rompel@univie.ac.at
LinkedIn\Rompel Group

