

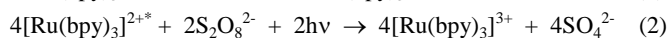
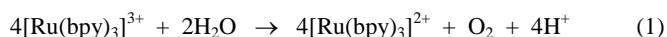
MULTI-ELECTRON-TRANSFER CATALYSTS NEEDED FOR SOLAR FUEL PRODUCTION

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A New Extremely Fast and Unusually Stable Molecular Catalyst for Water Oxidation

We have developed new vanadium-containing trivacant polytungstate ligands that can bind a central Co₄ unit to form a new water oxidation catalyst (WOC), **1**, that is very similar in structure to [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ (**Co4P2**), the WOC we reported last year.^{1,2} The latter catalyst is more reactive than the earlier tetra-ruthenium polyoxometalate (POM) WOC³⁻⁵ and is as fast as any WOC per active site metal reported to date. DFT B3LYP calculations show that unlike **Co4P2**, the frontier orbitals of **1** involve the central heteroatoms in the trivacant POM ligands. In other words, there is no involvement of phosphorus in the frontier orbitals of **Co4P2** but there is extensive involvement of vanadium in the frontier orbitals of **1**. Like **Co4P2**, **1** is oxidatively stable and hydrolytically stable over a wide pH range. However, **1** is *ca.* 16 times more reactive than **Co4P2** in dark water oxidation, eq 1 (conditions: 80 mM sodium borate buffer at pH 8.0, 1.0 mM [Ru(bpy)₃](ClO₄)₃ and 1.0 μM catalyst). In addition, **1** is *ca.* 5.1 times more reactive than **Co4P2** in light-driven water oxidation, eq 2 followed by eq 1 (conditions: 80 mM sodium borate buffer at pH 8.0, 1.0 mM [Ru(bpy)₃]Cl₂ photosensitizer, 5.0 mM Na₂S₂O₈ and 0.2 μM catalyst).



While these rates make **1** by far the most reactive molecular WOC to date and the stability of this catalyst at high pH seems to be at least as high as **Co4P2** it will take some time to quantify all the properties of **1** and its mechanism of water oxidation.

A POM catalyst for reduction of water and CO₂.

Effective (fast, selective and stable) catalysts for the reduction of H₂O to H₂ and CO₂ to CO and/or other reduced carbon species that are also compatible with aqueous media are sought. We have just developed a multi-Mn complex with vanadium-containing POM ligands. The X-ray crystallographic, spectroscopic, catalytic and stability properties of this new complex will be described.

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