# 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 $Co_4$ unit to form a new water oxidation catalyst (WOC), **1**, that is very similar in structure to $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**Co4P2**), the WOC we reported last year.[1,2] The latter catalyst is more reactive than the earlier tetra-ruthenium polyoxometalate (POM) WOC[3-5] 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 $[Ru(bpy)_3](ClO_4)_3$ 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 $[Ru(bpy)_3]Cl_2$ photosensitizer, 5.0 mM $Na_2S_2O_8$ and 0.2 μM catalyst).

$$4[Ru(bpy)_3]^{3+} + 2H_2O \rightarrow 4[Ru(bpy)_3]^{2+} + O_2 + 4H^+ \quad (1)$$

$$4[Ru(bpy)_3]^{2+*} + 2S_2O_8^{2-} + 2h\nu \rightarrow 4[Ru(bpy)_3]^{3+} + 4SO_4^{2-} \quad (2)$$

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 $CO_2$.**

Effective (fast, selective and stable) catalysts for the reduction of $H_2O$ to $H_2$ and $CO_2$ 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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**References**

(1) Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. *Science* **2010**, *328*, 342.
(2) Huang, Z.; Luo, Z.; Geletii, Y. V.; Vickers, J.; Yin, Q.; Wu, D.; Hou, Y.; Ding, Y.; Song, J.; Musaev, D. G.; Hill, C. L.; Lian, T. *J. Am. Chem. Soc.* **2011**, *133*, 2068.
(3) Geletii, Y. V.; Botar, B.; Kögerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 3896.
(4) Geletii, Y. V.; Huang, Z.; Hou, Y.; Musaev, D. G.; Lian, T.; Hill, C. L. *J. Am. Chem. Soc.* **2009**, *131*, 7522.
(5) Geletii, Y. V.; Besson, C.; Hou, Y.; Yin, Q.; Musaev, D. G.; Quinonero, D.; Cao, R.; Hardcastle, K. I.; Proust, A.; Kögerler, P.; Hill, C. L. *J. Am. Chem. Soc.* **2009**, *131*, 17360.