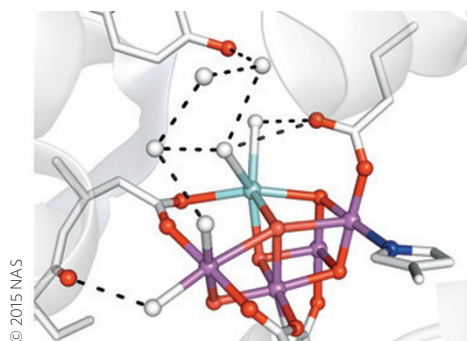


OXYGEN-EVOLVING COMPLEX

The state of manganese

Proc. Natl Acad. Sci. USA
<http://doi.org/38b> (2015)



The mechanism of the photosynthetic oxidation of water has proven difficult to elucidate. The formation of dioxygen from water is known to take place at the active site of the photosystem II enzyme — dubbed the oxygen-evolving complex (pictured) — which comprises a Mn_4CaO_5 cluster. This cluster's highest oxidation state is thought to promote O–O bond formation, but it

has remained challenging to characterize this species. Two mechanisms have been proposed for water oxidation and they both involve a high-valent manganese centre with a terminal oxido ligand. This moiety is thought to be either a Mn(IV)-oxyl radical or a Mn(V)-oxo species. Now, based on the combined experimental and theoretical study of three synthetic model compounds, a team of researchers led by Andrew Borovik at the University of California, Irvine, supports the involvement of a Mn(V)-oxo state.

The researchers prepared a mononuclear model that approximately mimics the Mn atoms at the centre of the oxygen-evolving complex; they used a trianionic ureaylate-based ligand (H_3buea^{3-}) that favours local C_3 symmetry around the manganese and provides an intramolecular hydrogen-bonding network. A Mn(III) complex was initially prepared and oxidized — with either one or two equivalents of ferrocenium — in order to better understand the properties of the model at higher oxidation states. This gave a series of three complexes that were each characterized by a combination of X-ray absorption and electron paramagnetic resonance

spectroscopy methods, as well as being analysed using density functional theory.

All three complexes adopt similar, high-spin mononuclear structures with the expected trigonal bipyramidal coordination geometry. Their molecular and electronic structures — including the covalent character of the Mn–O bonds and the spin density on the oxido ligand — concurred towards a Mn(III), a Mn(IV), and a Mn(V) complex, and provided no evidence for the presence a Mn(IV)-oxyl radical species. This means that the oxidation of Mn(III) occurs sequentially at the manganese centre, rather than at the ligand, and suggest that a high-spin Mn(V)-oxo moiety, similar to that seen in this study, may be at play in photosynthetic water oxidation. AP

PROTEOMICS

Profiling lipidated proteins

Angew. Chem. Int. Ed. <http://doi.org/f26s44> (2015)

The attachment of lipids to proteins — known as protein lipidation — can play an important role in the localization and function of proteins. One protein lipidation

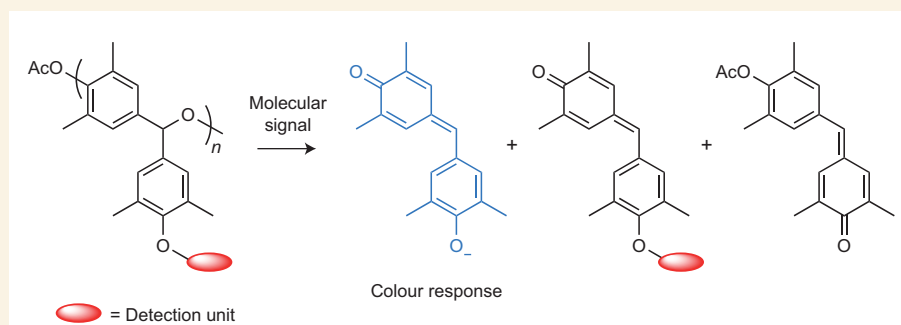
STIMULI-RESPONSIVE MATERIALS

Falling to pieces faster

J. Am. Chem. Soc. <http://doi.org/38c> (2015)

Self-immolative polymers are designed to fall apart in the presence of a specific physical or chemical signal. Typically, cleavage of an end group results in the sequential head-to-tail unzipping of the polymer chain. These materials can serve as effective detection systems because the depolymerization produces multiple copies of the same small molecule and thus amplifies the signal that triggered the process. Although this approach works well in solution, the solid state poses more of a challenge because very few chain ends are located at the surface of an object cast from such a polymer.

Now, a team of researchers at Pennsylvania State University led by Scott Phillips have overcome this limitation by designing a polymer in which each repeat unit — rather than just one chain end — contains a group that can trigger depolymerization. Because each polymer chain is functionalized along its length with these 'detection units', more of them remain accessible at the surface of a solid disk cast from them. Phillips and co-workers studied



two different systems — each based on a poly(benzyl ether) backbone — with either fluoride-responsive *tert*-butyldimethylsilyl (TBS) groups or Pd(0)-responsive allyl groups. Solution studies not only confirmed that these materials could be depolymerized with the appropriate triggers, but also that it occurs through a head-to-tail amplification process rather than the cleavage of each detection unit.

When a polymer with a TBS group on each repeating unit was cast into

a disk and placed into a solution of tetrabutylammonium fluoride, it took fewer than 5 hours for it to completely dissolve. In contrast, although a disk made from a polymer with just a single TBS unit at the end of each chain showed signs of some reaction in the first few hours (presumably arising from a small number of end groups at the solid surface), no further reaction was observed and the size of the disk remained unchanged after seven days. SC