Time-resolved studies reveal that DNA photo-oxidation by a Ru(II) polypyridyl complex is highly sensitive to the presence of modified bases.

Small changes in DNA structure, such as occur in point mutations or base-pair mismatches, can have significant biological effects. There is therefore great interest in developing molecules that can target specific base sites in DNA. Here we have studied the photo-oxidation of DNA by an intercalating ruthenium complex in a series of short sequences where selected guanine bases have been substituted with inosine (I). Time-resolved visible and IR studies reveal that, depending on which guanine is replaced, the yield of photo-oxidation can either increase or drastically decrease. It is proposed that these effects are due to favoured binding at inosine-containing sites. Similar behaviour is observed when IC is replaced with AT, indicating that the complex recognises these steps similarly. These experiments reveal how the photodynamics of a bound complex can be sensitive to changes in one nucleobase, and aid identification of the sites in DNA these compounds target.

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Vibrational sum frequency generation (VSFG) spectroscopy of electrocatalytic mechanisms

Here we demonstrate the use of vibrational sum frequency generation (VSFG) spectroscopy to study the mechanisms that occur during electrocatalysis. The 10 kHz broad-band VSFG experiment allows for detection of intermediates present at the surface with only 1 s data averaging. The ability to study short-lived species at electrode surfaces is important as many key intermediates may persist only transiently and be present either at the electrode surface itself or within the electric double layer.

In the study of electrocatalytic H2 evolution, we are able to identify the formation of a transition metal-hydride complex at the electrode surface even under conditions (low proton concentration) when such behaviour is unexpected. This is significant, as past studies using conventional techniques under similar conditions have struggled to detect this important intermediate, highlighting the advantage of being able to interrogate the electrode chemistry in situ.

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VSFG spectra showing how surface electrochemical events seen by the current-voltage response (left) can be monitored using VSFG spectroscopy (right) where we see new ν(CO) bands forming at the potentials of the electrochemical events.