

Ligand photodissociation in Ru (II)–1, 4, 7-triazacyclononane complexes enhances water oxidation and enables electrochemical generation of surface active species

Summary:

Although some ligand transformations involved in metal complexes have been reported during water oxidation (WO) ((photo)chemical/electrochemical), such as ligand decomposition, partial oxidation, or complete dissociation, ligand photodissociation has not been reported yet. Here, we report the first example of ligand photodissociation in $[\text{Ru}([\text{9}]\text{-aneN3})(\text{bpy})(\text{DMSO})]^{2+}$, **1** (bpy is 2,2'-bipyridine), under the frequently used conditions for screening water oxidation catalysts, and its relation to the catalyst activity. We demonstrate that the observed photodissociation in complex **1** boosts its catalytic performance towards electrochemical WO and enables surface generation of electrochemically active species. Conversely, the absence of such a phenomenon in $[\text{Ru}([\text{9}]\text{-aneN3})(\text{pic})(\text{DMSO})]^+$, **2** (pic is 2-picolinate), resulted in an unreactive catalyst towards WO. DFT calculations could explain the observed difference between complexes **1** and **2** aqueous solutions towards ligand partial-dissociation when exposed to light based on the activation barrier between triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) and dissociative metal-centered (^3MC) excited states as well as the stability of the ^3MC state. Whereas the $^3\text{MLCT}$ – ^3MC transition for complex **2** requires higher activation energy than that for complex **1**, the resulting ^3MC state is less stable than its $^3\text{MLCT}$ state. Calculations involving the ligand exchange process reveal that a water molecule can replace one of the pyridine rings with a considerably lower activation barrier in the triplet state as compared to the singlet state. These findings suggest the possible light-assisted ligand photodissociation as a new strategy towards catalyst activation offering a key advancement in water oxidation catalysis. The light-assisted ligand exchange process is found to be more feasible than the thermal ligand exchange process.

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