

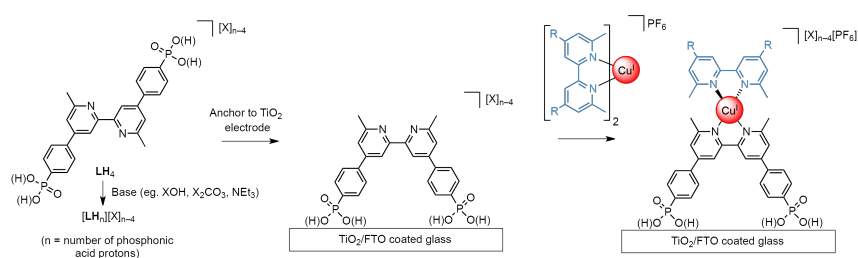
## The Influence of Phosphonic Acid Protonation State on the Efficiency of Bis(diimine)copper(I)-based Dye Sensitized Solar Cells

A. J. Stephens<sup>1</sup>, F. J. Malzner<sup>1</sup>, E. C. Constable<sup>1</sup>, C. E. Housecroft<sup>1</sup>

<sup>1</sup>University of Basel

The photoactive component of a Dye-Sensitized Solar Cell (DSC) consists of a dye molecule bound (either electrostatically or covalently) to a mesoporous TiO<sub>2</sub> surface through functional groups such as phosphonic acids.<sup>[1]</sup> Here, we investigate how the protonation state of such phosphonic acids affects their ability to anchor to TiO<sub>2</sub> substrates, and how the operational parameters of the resultant DSCs are influenced in turn.

Stepwise titration of bases into a solution of LH<sub>4</sub> alters the ligands protonation state and the nature of its associated cations to give [LH<sub>n</sub>][X]<sub>n-4</sub> (Fig. 1). The formation of Cu(I) dye molecules is achieved by sequentially exposing TiO<sub>2</sub> electrodes to [LH<sub>n</sub>][X]<sub>n-4</sub>, followed by the homoleptic Cu(I) complex of the ancillary ligand. Our results demonstrate that the addition of a small amount of base to LH<sub>4</sub> (~1 eq) can afford up to a 30% increase in DSC efficiency. These results are rationalized through consideration of proton / cation transfer from the ligand to the surface, deprotonation of surface hydroxides, and changes in the photochemical and electrochemical properties of ligand LH<sub>4</sub> upon deprotonation.



**Figure 1.** The sequential formation of a bis(diimine)copper(I) dye on a TiO<sub>2</sub> electrode using phosphonic acids in different protonation states.

[1] C. E. Housecroft, E. C. Constable, *Chem. Soc. Rev.*, **2015**, 44, 8386–8398.