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

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The photoactive component of a Dye-Sensitized Solar Cell (DSC) consists of a dye molecule bound (either electrostatically or covalently) to a mesoporous TiO_2 surface through functional groups such as phosphonic acids.[1] Here, we investigate how the protonation state of such phosphonic acids affects their ability to anchor to TiO_2 substrates, and how the operational parameters of the resultant DSCs are influenced in turn.

Stepwise titration of bases into a solution of LH_4 alters the ligands protonation state and the nature of its associated cations to give $[LH_n][X]_{n-4}$ (Fig. 1). The formation of Cu(I) dye molecules is achieved by sequentially exposing TiO_2 electrodes to $[LH_n][X]_{n-4}$, 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_4 (~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_4 upon deprotonation.

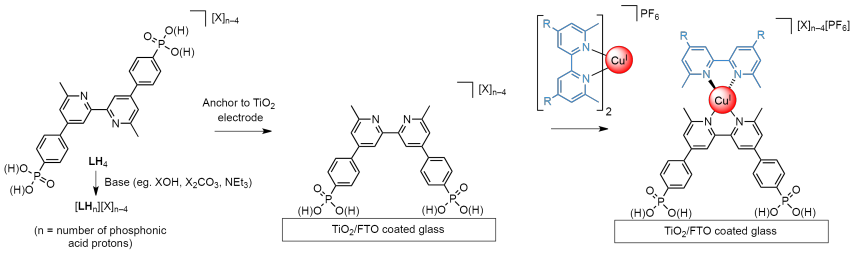

Figure 1. The sequential formation of a bis(diimine)copper(I) dye on a TiO_2 electrode using phosphonic acids in different protonation states.

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