

Modifying spacers and anchoring groups for heteroleptic Cu(I) - 6,6'-dimethyl-2,2'-bipyridine based DSSCs

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Heteroleptic $[\text{Cu}(6,6'\text{-dimethyl-2,2'\text{-bipyridine}})_A(6,6'\text{-dimethyl-2,2'\text{-bipyridine}})_C]^+$ (A: anchoring ligand, C: capping ligand) complexes in which the bpy units are functionalized in the 4- and 4'-positions are known to be good light harvesting materials in dye-sensitized solar cells (DSSCs). When the formation of isolated heteroleptic $[\text{Cu}(\text{bpy})_A(\text{bpy})_C]^+$ complexes is attempted, equilibration occurs giving mixtures of homo- and heteroleptic complexes; separation is very difficult. Therefore our group has developed a stepwise build-up of DSSCs (Figure 1a): a 'surface-as-ligand, surface-as-complex' approach. For the first step a 6,6'-dimethyl-2,2'-bipyridine ligand, which is modified in the 4 and 4'-positions by a spacer bearing an anchoring group (e.g. 4-phenylphosphonic acid, Figure 1b) is bound to a TiO_2 surface. Afterwards Cu(I) and a capping ligand are introduced by a ligand exchange reaction between the anchored bpy_A and a bpy_C of the homoleptic $[\text{Cu}(\text{bpy})_2]^+$ complex. In previous work done by our group, much focus was put on the modification of the capping ligand to enhance photo to current efficiencies. The standard anchoring ligand with the best performance, which is currently used in our group is shown below. Changing the anchoring group from phosphonic acid to alternative groups¹, as well as modifying the phenyl spacer to a thiophene spacer has been investigated² with a goal of enhancing solar cell performance for $[\text{Cu}(\text{bpy})_2]^+$ complexes. Targets are to gain better affinity of the anchoring group to TiO_2 , better electron transport through the spacer, less electron recombination between dye and electrolyte and an overall longer electron lifetime within the complex.

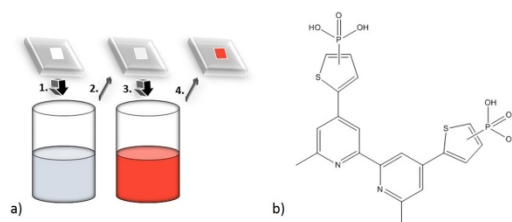


Figure 1: a) Stepwise build of heteroleptic Cu(I) - DSSCs. b) Anchoring ligand for Cu(I) - DSSCs.

[1] Y. Baumgartner, Y. Maximilian Klein, E. C. Constable, C. E. Housecroft and M. Willgert, *RSC Adv.*, **2016**, 6, 86220–86231.

[2] Y. M. Klein, M. Willgert, A. Prescimone, E. C. Constable and C. E. Housecroft, *Dalt. Trans.*, **2016**, 45, 4659–4672.