Are Alkynyl Spacers in Ancillary Ligands in Heteroleptic Bis(diimine)copper(I) Dyes Beneficial for Dye Performance in Dye-Sensitized Solar Cells?

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Author(s) Risi, Guglielmo; Becker, Mariia; Housecroft, Catherine E.; Constable, Edwin C.
Author(s) at UniBasel Housecroft, Catherine ; Constable, Edwin Charles ; Becker, Mariia ; Risi, Guglielmo ;
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The syntheses of 4,40 -bis(4-dimethylaminophenyl)-6,60 -dimethyl-2,20 -bipyridine (1), 4,40 -bis(4-dimethylaminophenylethynyl)-6,60 -dimethyl-2,20 -bipyridine (2), 4,40 -bis(4- diphenylaminophenyl)-6,60 -dimethyl-2,20 -bipyridine (3), and 4,40 -bis(4-diphenylaminophenylethynyl)- 6,60 -dimethyl-2,20 -bipyridine (4) are reported along with the preparations and characterisations of their homoleptic copper(I) complexes [CuL2][PF6] (L = 1 -4). The solution absorption spectra of the complexes exhibit ligand-centred absorptions in addition to absorptions in the visible region assigned to a combination of intra-ligand and metal-to-ligand charge-transfer. Heteroleptic [Cu(5)(Lancillary)]+ dyes in which 5 is the anchoring ligand ((6,60 -dimethyl-[2,20 -bipyridine]- 4,40 -diyl)bis(4,1-phenylene))bis(phosphonic acid) and Lancillary = 1 -4 have been assembled on fluorine-doped tin oxide (FTO)-TiO2 electrodes in dye-sensitized solar cells (DSCs). Performance parameters and external quantum e ciency (EQE) spectra of the DSCs (four fully-masked cells for each dye) reveal that the best performing dyes are [Cu(5)(1)]+ and [Cu(5)(3)]+ . The alkynyl spacers are not beneficial, leading to a decrease in the short-circuit current density (JSC), confirmed by lower values of EQEmax . Addition of a co-absorbent (n -decylphosphonic acid) to [Cu(5)(1)]+ lead to no significant enhancement of performance for DSCs sensitized with [Cu(5)(1)]+ . Electrochemical impedance spectroscopy (EIS) has been used to investigate the interfaces in DSCs; the analysis shows that more favourable electron injection into TiO2 is observed for sensitizers without the alkynyl spacer and confirms higher JSC values for [Cu(5)(1)]+
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