

## Copper Complexes for Dye-sensitized Solar Cells

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Redox mediators in dye sensitized solar cells (DSCs) or hole transport materials (HTMs) in solid state DSCs (ssDSCs) play a major role determining the photocurrent and the photovoltage. To maintain the photocurrent, the reduction of oxidized dye by the redox mediator should be significantly faster than the back electron transfer between TiO<sub>2</sub> and the oxidized dye. The driving force for dye regeneration with the redox mediator should be sufficiently low to provide high photovoltages. With the introduction of new copper complexes as promising redox mediators or HTMs in DSCs both criteria are satisfied to enhance power conversion efficiencies and stability.<sup>1</sup>

Due to the small reorganization energy between Cu(I) and Cu(II) species, this copper complexes can sufficiently regenerate the oxidized dye molecules with close to unity yield at driving force potentials as low as 0.1V. The high photovoltages of over 1.0 V were achieved by the series of copper complex based redox mediators without compromising photocurrent densities. The solar-to-electrical power conversion efficiencies for [Cu(tmby)<sub>2</sub>]<sup>2+/1+</sup>, [Cu(dmby)<sub>2</sub>]<sup>2+/1+</sup> and [Cu(dmp)<sub>2</sub>]<sup>2+/1+</sup> based electrolytes were 10.3%, 10.0% and 10.3%, respectively, using the organic Y123 dye under AM1.5G illumination.<sup>2,3</sup> Solar cells that operate efficiently under indoor lighting are of great practical interest as they can serve as electric power sources for portable electronics and devices for wireless sensor networks or the Internet of Things. Our photosystem combines two judiciously designed sensitizers, coded D35 and XY1, with the copper complex Cu(II/I)(tmby) as a redox shuttle (tmby, 4,4',6,6'-tetramethyl-2,2'-bipyridine), and features a high open-circuit photovoltage of 1.1 V. The DSC achieves an external quantum efficiency for photocurrent generation that exceeds 90% across the whole visible domain from 400 to 650 nm, and achieves power outputs of 15.6 and 88.5 μW cm<sup>-2</sup> at 200 and 1,000 lux, respectively, under illumination from a model Osram 930 warm-white fluorescent light tube. This translates into a PCE of 28.9%.<sup>5</sup>

Until recently, there have been no viable alternatives for Spiro-OMeTAD as a hole-transport material (HTM) for ssDSCs. We show that copper coordination complexes in the solid phase can act as efficient molecular hole conductors in DSCs. We report a record 11% stable solid-state molecular photovoltaic based on copper complex HTM under standard AM1.5G conditions. We demonstrate that rapid hole hopping and the amorphous state of copper complexes are pivotal for achieving such a high conversion efficiency in the solid-state molecular photovoltaics.<sup>4</sup>

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