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### **Introduction**

The current need for renewable energy sources and particularly photovoltaic technologies has led to a massive worldwide research effort. One of their success stories started exactly 25 years ago when Grätzel and coworkers introduced dye-sensitized solar cells (DSCs) as a new emerging technology.<sup>[1-3]</sup> DSCs are based on the premise that illuminated chromophores can inject electrons into a nanostructured semiconductor electrode to enable direct sunlight to electricity conversion. Low-cost materials, scalable manufacturing with low investment costs, promising designs using multiple colors and patterns. DSCs represent a complex system and research efforts mainly focused on tailoring the physiochemical and photochemical aspects of their main components, for instance the dyes at the mesoporous semiconductor, the redox mediator in the liquid electrolyte or the solid hole transport material.

### **Structure and Working Principles of DSCs**

The working principles of DSCs contrast any other solid-state junction solar cells. Here, dye molecules are adsorbed as a monolayer on transparent, mesoporous wide band gap semiconductor, most commonly TiO<sub>2</sub> (anatase), deposited on conducting glass (fluorine doped tin oxide layer, FTO).<sup>[4]</sup> Subsequent to photoexcitation (1), the dye injects (2) an electron into the conduction band of the semiconductor (3). The dye is regenerated (4) by the electron donation from the liquid redox mediator or solid hole transport material, which is restored to its initial state at the counter electrode (5). The counter electrode is loaded with a catalyst, such as platinum, graphene or PEDOT. The photogenerated electrons can flow from the photoanode through an external circuit, perform work and reach the counter electrode. Competing and limiting processes might diminish the performance of DSCs. The photoexcited electrons could recombine with the redox couple (a) or the dye simply relaxes to the ground state through radiative or non-radiative pathways (b). The injected electron can be intercepted directly by the redox mediator from the semiconductor (c).

The redox couple is a key component in liquid electrolyte-based DSCs for dye regeneration and charge transport between the two electrodes. Finding an efficient, non-corrosive electron-transfer mediator is an important step towards higher efficiency and the industrialization of DSCs.<sup>[5]</sup> The iodide/triiodide redox shuttle, as an unparalleled option for efficient electrolytes of DSCs. The biggest disadvantage is the low redox potential, preventing attainment of a high open-circuit voltage. A large potential loss results from the energetic mismatch between the redox couples and the sensitizers (S<sup>+</sup>/S). Upon excitation it should inject electrons into the solid with a quantum yield of unity.

### **Copper Complexes as Redox Mediators**

In the early 2000s, Fukuzumi and Bignozzi reported that copper complexes worked well as redox mediators at reduced light intensities (~20 mWcm<sup>-2</sup>). The bis(2,9-dimethyl-1,10-phenanthroline) copper (Cu(dmp)<sub>2</sub>) based DSCs were further improved by Wang et al. by combining them with an organic sensitizer, which led to an increase in the PCE-efficiencies from 7.0 % at 100 mWcm<sup>-2</sup> to 8.3 % at ~23 mWcm<sup>-2</sup> AM 1.5G light.<sup>[6]</sup> With further improvement of DSCs and introduction of new copper based redox shuttles, Freitag et al. recently surpassed the 10.0% efficiency mark at 100 mWcm<sup>-2</sup>AM 1.5G light for this family

of alternative redox mediators. The important achievement of the copper based electrolytes is that they are able to successfully regenerate the dye near quantitatively with a very small driving force of 0.1 V. For this reason, the copper based mediators are perceived to be responsible for the next expected efficiency jump in DSCs.

### Copper Complexes as Hole Transport Materials

Other HTMs based on organic small molecules or conducting polymers are less efficient to date. Inorganic wide-bandgap p-type semiconductors such as CuSCN and CuI show higher conductivity than their organic counterparts, but yielded thus far lower PCE in ssDSC devices. More recently, the dark-colored Sn<sup>4+</sup> compound Cs<sub>2</sub>SnI<sub>6</sub> was successfully used as a hole conductor in ssDSC, reaching PCE-values of up to 7.8 %.<sup>[7]</sup> Interestingly, the open-circuit potentials for ssDSC that use inorganic p-type semiconductors is thus far significantly lower (~0.6 V) than that obtained with spiro-OMeTAD (~0.9 V).

Recently a new type of HTM was discovered, based on earth abundant and very stable copper complexes in solid-state DSC, resulting in record-breaking solar cell efficiencies.<sup>[8]</sup> Considering the rapid electron self-exchange rate in rigid copper complexes, [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup> molecules were used as an HTM for solid-state DSCs (ssDSCs). The so called “zombie” ssDSCs were simply made by evaporating volatile solvents from the [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup> redox shuttle electrolyte in ambient air. The ssDSC showed a high short-circuit photocurrent (J<sub>sc</sub>) of 15.8 mA/cm<sup>2</sup>, exceeding the J<sub>sc</sub> of a liquid electrolyte based DSC (10.4 mA/cm<sup>2</sup>). The PCE of the ssDSC was 11.2% under standard AM1.5G conditions, a performance superior to those of counterparts made using CuSCN (2%), CuI (4.5%), or cobalt complexes as HTMs.<sup>[9]</sup> Current solid hole transport materials still face some major challenges in terms of efficiency with low J<sub>sc</sub>. Even if they are solution processed, the pore filling problem is difficult to overcome and can never be completed when solvent evaporates living space, which greatly influences charge separation and collection.

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