Modifiying anchors to improve the performance of sustainable copper-based dye-sensitised solar cells

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Abstract

Copper-based dye-sensitised solar cells (DSSCs) are solar cells consisting of a semiconductor (TiO_2), which can be modified by a dye, in this case a copper-dye, which enables absorption and transformation of photons into electrical energy. Compared to other types of solar cells, these DSSCs take advantage of non toxic and low cost materials and show good light harvesting abilities. The centerpiece of a copper DSSC is a heteroleptic complex with a copper(I) metal-ion coordinated by two organic ligands. Copper(I) is the metal of choose as it is very abundant in the earth crust and very cost efficient compared to ruthenium, the metal for the best metal based DSSCs so far. One organic ligand possesses a group to anchor to the TiO_2 semiconductor and the capping ligand has features to stabilise the complex and push electrons towards the semiconductor. In this work we will focus on the anchoring ligand by changing spacers as well as the anchoring group itself to enhance the performance of these sustainable DSSCs.

Introduction

Dye-sensitized solar cells (DSSCs) consist of a dye, which can be adsorbed on a nanoporous TiO_2 semiconductor surface. Their ability to absorb photons under irradiation and transform them into separated charges is the main feature these materials possess. The generated electrons can be injected into the TiO_2 semiconductor to generate electric power. The first DSSC was constructed in 1991 by O'Regan and Grätzel.[1] They used a Ruthenium(II)-complex as a dye to modify the TiO_2-surface. Since this report the variety of dyes, electrolytes and electrode-materials has increased tremendously. These days, DSSCs can be divided into organic and inorganic sensitizers. Organic dyes show promising performance with efficiencies of over 10 %[2] and Ru(II)-based inorganic dyes reach values of up to 11%[3]. The main drawback for purely organic dyes is their often very complicated and thus expensive synthesis, whereas inorganic dyes are easier accessible by coordination reactions of metal salts with organic ligands. Nevertheless the most used metal ruthenium is very rare and expensive. For this reason our group focusses on dyes based on copper(I), which is more abundant and a very cost efficient alternative.

A DSSC consists of 3 main components (figure 1). The working electrode is a fluorine doped tin-oxide (FTO) glass plate. On this conductive FTO layer, a second layer of nanoporous TiO_2 is printed, which is later modified by an absorbed dye. The counter-electrode is a FTO coated glass with a thin platinum layer on top. These two electrodes are connected by an I^{3-}/I^- based liquid electrolyte in between.

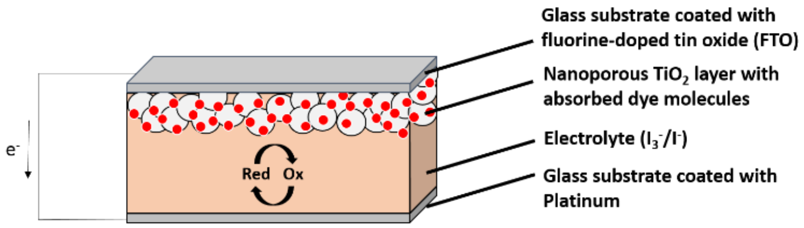
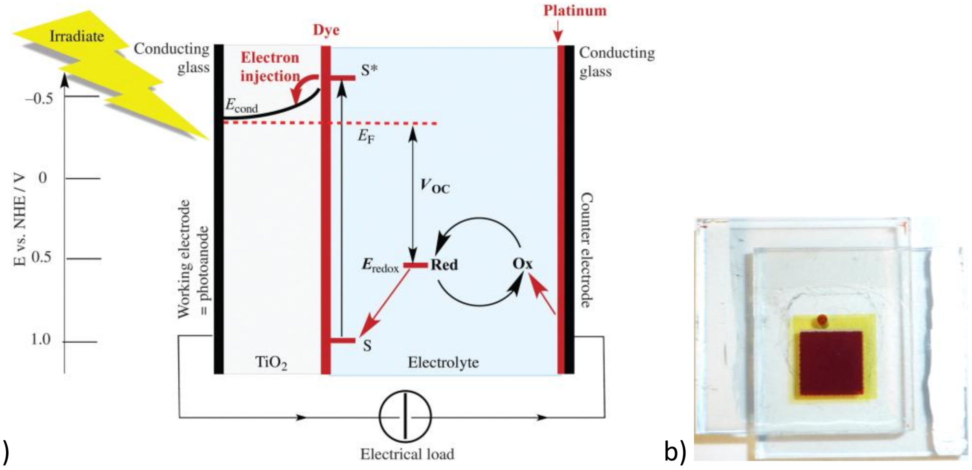


Figure 1. The design principle of a DSSC with the nanoporous TiO2 working-electrode at the top and the Pt-counter-electrode at the bottom. In between a liquid I^{3-}/I^- based electrolyte is added.

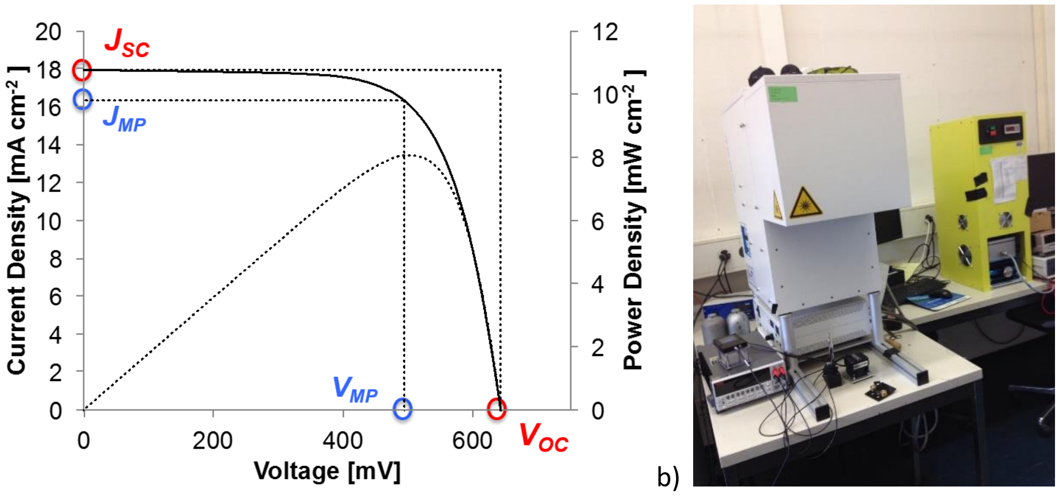
The working principle of a DSSC is shown in figure 2. Upon irradiation, the dye, absorbed on the nanoporous TiO_2-semiconductor, absorbs a photon and excites an electron into a higher energetic state. From this excited state the electron can be injected into the semiconductor and travels through an external circuit to the counter-electrode. The oxidised dye molecule is reduced by the I^{3-}/I^- redox couple present in the electrolyte. In the last step the oxidised electrolyte gets reduced by the platinum counter-electrode and the electric circle is closed.



a) b)

Figure 2. a) Working principle of a DSSC with the working electrode (TiO_2) on the left and the counter-electrode on the right side. The dye is present in its ground (S) and excited state (S*). b) A final DSSC built in our laboratory.

The overall performance of a DSSC is measured on a sun simulator (figure 3b), which exhibits an irradiation of one sun (1000W/cm^2). The solar cell (figure 2b) is placed under the light source and a J/V measurement (figure 3) is performed, where an external voltage is applied to the solar cell and sweeped form -0.1 V to 0.7 V. At each V-point the current density the solar cell produces is measured and a J/V curve is obtained. From this curve important values like the open-circuit voltage (V_{OC}), the short-circuit current (J_{SC}), the fill factor (ff) and the overall efficiency (η) can be obtained.



a) b)

Figure 3. a) J/V-curve measured on a sun simulator. b) Two sun simulators currently used in our lab.

Our group is using a design and production principle of Cu(I)-dyes based on a stepwise on-surface modification (figure 4 a). In the first step the blank TiO_2-electrode is dipped into an anchoring ligand solution. The ligand will bind to the surface and stay there. The anchoring ligand modified electrode is placed in a dye bath of a homoleptic Cu(I)-dye. In this step a ligand exchange reaction occurs. One ligand of the homoleptic complex is cleaved and replaced by the anchoring ligand attached to the surface. This way it is possible to form heteroleptic Cu(I) complexes, which is not possible in situ. Figure 4 b shows the general features (anchoring groups and spacers) of a heteroleptic dye on the TiO_2 surface, which will be addressed in the next sections.

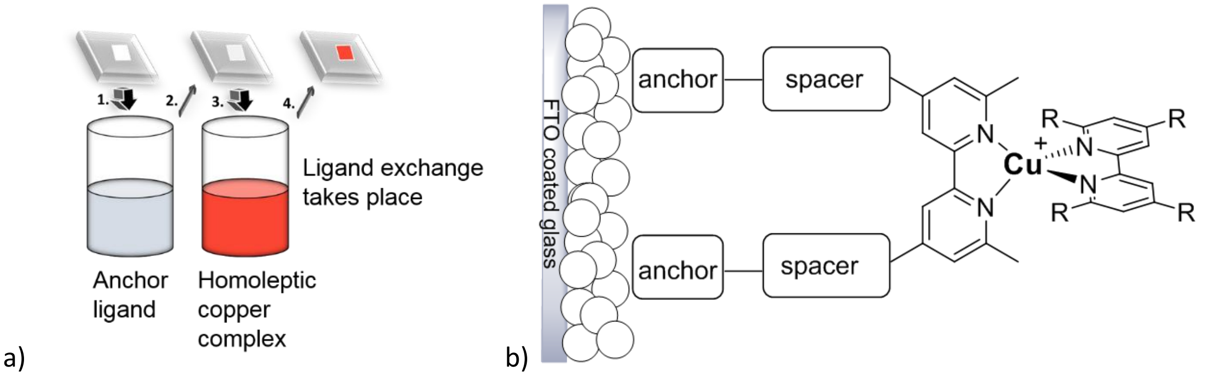


Figure 4. a) Stepwise assembly of heteroleptic Cu(I) dyes on TiO_2. b) structural features of the ligands, which will be addressed in the next paragraph.

Changing the spacer[4]

In this first study we investigated the effect of changing the spacer of the standard anchoring ligand (**1**) from a phenyl group towards a thiophene group. In addition we tested the effect of the position of the phosphonic-acid anchoring group on the thiophene. We compared the efficiencies of the new synthesised anchoring ligands, combined with three different capping ligands (figure 5)[4].

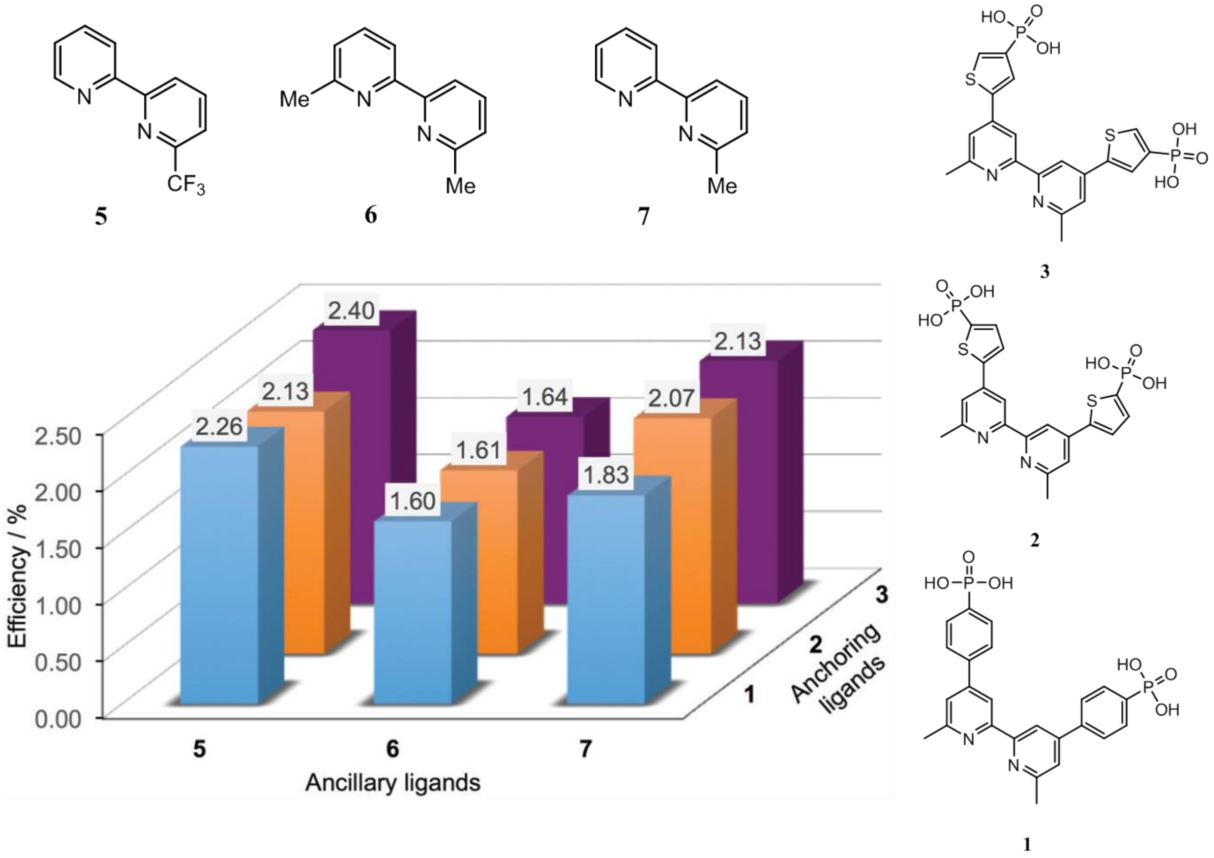


Figure 5. Efficiencies of DSSC with three different anchoring ligands (**1-3**) combined with three different capping ligands (**5-7**).

The best performing dye of this series used anchoring ligand **3** with a thiophene spacer and the anchoring group in 4-position combined with capping ligand **5** from a previous study[5].

An efficiency of 2.4 % equals 41.7 % efficiency relative to the reference Ru(II)-dye N719, showing the good potential of these materials.

Changing the spacer[6]

In the second big study we synthesised 4 new anchoring ligands for Cu(I)-based DSSCs. In addition to the standard ligand core 6,6'-Dimethyl-2,2'-bipyridine (bpy, in ligands **9** and **11**) we introduced the ridged 2,9-Dimethyl-1,10-phenanthroline core (phen, in ligand **8** and **10**). Both ligand cores were modified by introducing either a cyanoacrylic acid (**8** and **9**) or a cyanophosphonic acid (**10** and **11**) anchoring group. The results displayed in figure 6 highlight the beneficial effect of the bpy over the phen core, as well as the big influence of the anchoring group on the solar cell performance. Dyes using the new cyanophosphonic acid anchoring group show the best efficiencies.

Experiment Dye	Jsc [mA/cm2]	Voc [mV]	FF [%]	Eta [%]
[Cu(**8**)(6)]+	1.06	412	71	**0.31**
[Cu(**8**)(6)]+	1.59	410	72	**0.47**
[Cu(**9**)(6)]+	2.01	388	49	**0.38**
[Cu(**9**)(6)]+	2.61	424	54	**0.60**
Experiment Dye	**Jsc [mA/cm2]**	**Voc [mV]**	**FF [%]**	**Eta [%]**
[Cu(**10**)(6)]+	2.95	423	72	**0.90**
[Cu(**10**)(6)]+	3.06	421	72	**0.93**
[Cu(**11**)(6)]+	4.67	511	73	**1.75**
[Cu(**11**)(6)]+	5.09	511	73	**1.91**

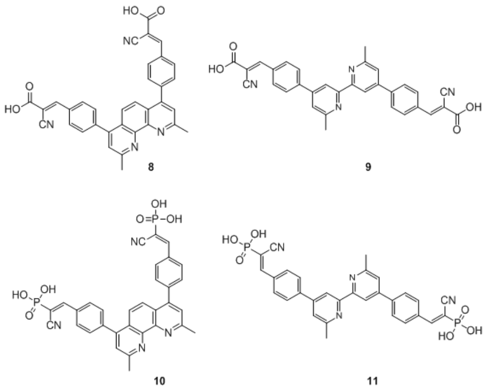


Figure 6. Results of solar cell measurements combining four new anchors (**8-11**) with capping ligand **6**.

The best anchor of this study was compared with the standard anchor **1**, using capping ligand **5** to obtain solar cells with efficiencies of over 2.5 % (figure 7). The best performing dye of this study was using the new anchoring ligand **11** with capping ligand **5** and showed an efficiency of 2.56 % (42.6 % relative to Ru(II)-reference N719)[6].

Experiment Dye	Jsc [mA/cm2]	Voc [mV]	FF [%]	Eta [%]
[Cu(**1**)(5)+]	6.30	585	68	**2.51**
[Cu(**1**)(5)+]	6.01	576	66	**2.28**
[Cu(**11**)(5)+]	6.59	547	71	**2.56**
[Cu(**11**)(5)+]	6.59	548	70	**2.52**

Figure 7. Results of solar cell measurements comparing anchors **1** and **11**, both using **5** as capping ligand.

Conclusion

In the studies towards new anchoring ligands for sustainable Cu(I) based DSSC we synthesised 6 new anchoring ligands and compared their performance with the standard anchor 1. The first study showed the beneficial effect of thiophene spacers and the second study showed the big impact a cyanophosphonic acid anchoring group has on the performance of these DSSCs. By using knowledge gained from both studies and further modifying the anchoring ligand and/or the capping ligand, the efficiency of these non-toxic and environmentally friendly solar cells can be further improved.

Acknowledgments

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