Organic Dye for Highly Efficient Solid-State Dye-Sensitized Solar Cells**

By *Lukas Schmidt-Mende*,* *Udo Bach*,
Robin Humphry-Baker, *Tamotsu Horiuchi*,
Hidetoshi Miura, *Seigo Ito*, *Satoshi Uchida*, and
Michael Grätzel

Dye sensitized solar cells are an interesting low cost alternative to conventional solar cells. Efficiencies over 10 % have been achieved.[1,2] Advantageous is the replacement of the liquid electrolyte in these devices with a solid charge carrier material to avoid any sealing and long term stability problems. In 1998 Bach et al.[3] demonstrated that the electrolyte can be replaced by a hole conductor. Here we report a very efficient solid state solar cell with the amorphous organic hole transport material 2,2′,7,7′ tetrakis (*N*,*N* di *p* methoxyphenyl amine)9,9′ spirobifluorene (spiro OMeTAD) as hole conductor and for the first time an organic metal free indoline dye as sensitizer. Record efficiencies for this type of cell of over 4 % over the solar spectrum were reached.

Until now, sensitization using organic dyes has not been as efficient as using ruthenium dyes, which have been successfully applied previously. Metal free dyes such as perylene derivatives,[4] coumarin dyes,[5] porphyrin dyes,[6] and cyanine and merocyanine dyes[7] have been used as sensitizers, but did not achieve the same solar conversion efficiency as ruthenium dyes. The efficiencies achieved in this work with the indoline dye (D102) are even higher than the highest currently reported values for ruthenium dye sensitized solid state cells. In addition, this dye has the advantage that it can be produced at low cost, because it does not contain the expensive rare metal ruthenium and it is easy to synthesize.

Up to now the best results reported with spiro OMeTAD as a hole conductor are efficiencies of 3.2 %.[8] In that work the dye uptake and open circuit voltage were optimized by a silver complexation. In the case of the indoline dye we were able to reach an efficiency of just over 4 % without further optimization. This shows the extremely high potential of the indoline dye as a sensitizer in solid state dye sensitized solar cells. Indoline dyes have previously been used in dye sensitized solar cells with a liquid electrolyte.[9,10] There also they showed a good performance of up to $\eta = 6.1$ % conversion efficiency compared to 6.3 % for a N3 dye sensitized cell.[9] Solid state devices usually have a lower performance, which is not the case here with an extraordinary efficiency of 4 %, which approaches that of their liquid electrolyte counterpart.

Figure 1a shows the chemical structure of the indoline dye D102 and spiro OMeTAD (Fig. 1b), the organic compounds used in this work.

The dye D102 has a very strong absorption coefficient (55 800 L mol^{-1}cm^{-1} at 491 nm), which is four times stronger than the previously used ruthenium dye N3 (13 900 L mol^{-1}cm^{-1} at 541 nm).[9] This makes it of especial interest for solid state devices, where the film thickness is crucial. Our results show an optimized film thickness of the active nanoporous TiO_2 layer of ~1.6 μm. This is thinner than for the cells sensitized with N719, where a thickness of ~2 μm seems to be ideal.[11] The optimization can be explained by a tradeoff of light harvesting and series resistance. Thinner devices have a lower series resistance, but a smaller fraction of the incoming light is absorbed within the film. In thicker nanoporous TiO_2 layers the series resistance becomes more dominant, because of the limitation of the charge carrier mobility in common organic hole conductors, such as spiro OMeTAD. This leads to more charge carrier recombination. In both cases the overall efficiency drops. With the higher molar extinction coefficient of the new dye we can fabricate thinner TiO_2 layers and still absorb enough of the incoming light for efficient cells.

The structure of our cells is schematically shown in Figure 1c. The cells consist of a F doped SnO_2 conduction glass substrate onto which a compact TiO_2 layer was deposited by spray pyrolysis. This is necessary to avoid direct contact between the hole conductor and the SnO_2, which would enable direct charge carrier recombination at this interface. The nanoporous TiO_2 layer was deposited by doctor blading. This method allowed us to produce homogeneous nanoporous TiO_2 films with controlled thickness. After the TiO_2 layer had been sintered, it was sensitized with D102 by soaking the

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[*] Dr. L. Schmidt-Mende, Dr. U. Bach, Dr. R. Humphry-Baker,
Dr. S. Ito, Prof. M. Grätzel
Institut des Sciences et Ingénierie Chimiques (ISIC)
Laboratoire de Photonique et Interfaces (LPI)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
CH-1015 Lausanne (Switzerland)
E-mail: lukas.schmidt-mende@epfl.ch

Dr. T. Horiuchi, Dr. H. Miura
Technology Research Laboratory, Corporate Research Center
Mitsubishi Paper Mills Limited
46, Wadai, Tsukuba City, Ibaraki 300-4247 (Japan)

Dr. Satoshi Uchida
Institute of Multidisciplinary Research for Advanced Materials (IMRAM)
Tohoku University
1-1 Katahira 2-chome, Aoba-ku, Sendai 980-8577 (Japan)

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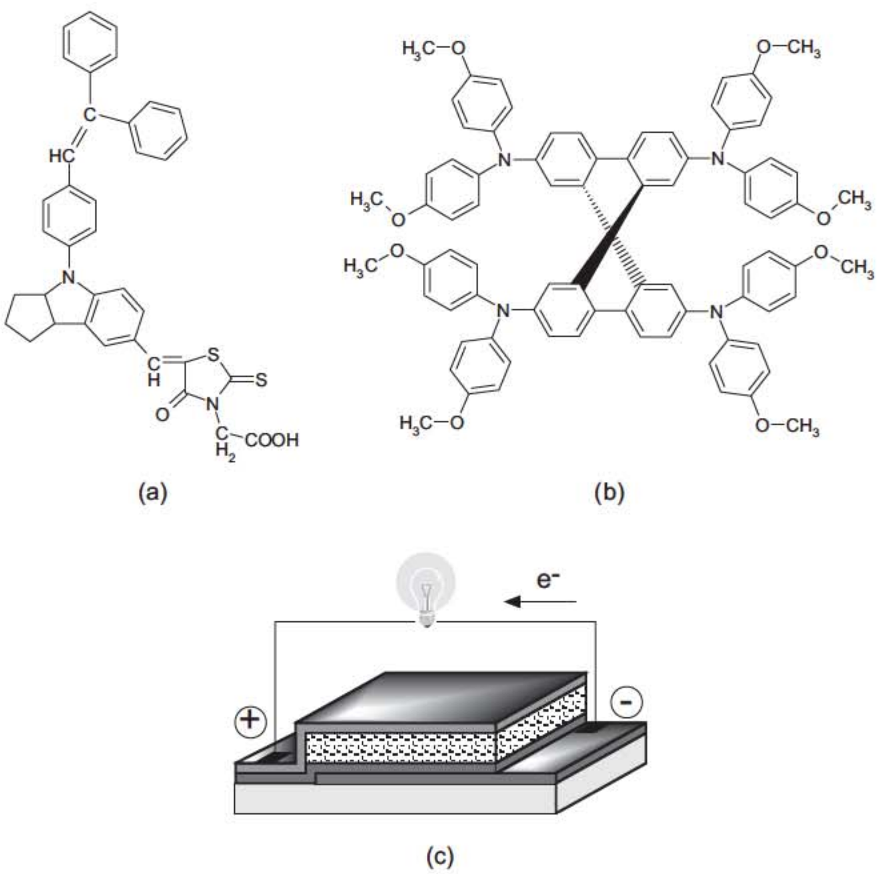

Figure 1. a) Structure of the indoline dye molecule. b) Structure of the hole conductor spiro-OMeTAD. c) Device structure: F-doped SnO_2-covered glass substrate with a thin (<100 nm) dense TiO_2 layer, a nanoporous TiO_2 layer covered with dye and filled with spiro-OMeTAD, and 30 nm Au electrode on top.

substrate in a 0.5 mM *tert* butanol/acetonitrile (1:1) dye solution for an hour. The hole conductor matrix was applied by spin coating of a solution of spiro MeOTAD in chlorobenzene, containing $Li[CF_3SO_2]_2N$, *tert* butylpyridine (^{t}BP) and $N(PhBr)_3SbCl_6$. Before spin coating this solution was deposited on the dye sensitized substrate and was allowed to penetrate into the pores of the TiO_2 layer for 1 min. Next the devices were dried for 30 min in an argon flow and then finished by being placed under vacuum ($\sim 5 \times 10^{-6}$ mbar) and having a 30 nm gold electrode evaporated on top.

Figure 2a shows the absorption properties of TiO_2 electrodes sensitized with the indoline dye D102 and the ruthenium dye N719 prior to the evaporation of the top gold electrode. The light harvesting properties of the D102 sensitized electrode are greatly superior to the N719 sensitized electrode. Despite its lower film thickness of 1.6 µm, compared to the N719 sensitized TiO_2 electrode of 2.0 µm, it absorbs more then 90 % of the incident light over a wide range of the visible spectrum (440 550 nm). The incident photon to electron conversion efficiency (IPCE) in this wavelength range is about 60 %. As the absorption of light in this range is close to 100 % we can estimate the absorbed photon to electron conversion efficiency to be close to 60 %. The solar cell sensitized with the ruthenium dye N719 shows a peak IPCE of just over 60 % at 510 nm, but its IPCE value is below that of the indoline sensitized sample over most of the spectral range. In order to estimate the absorbed photon to electron conversion efficiency in the final device, the reflecting properties of the top gold electrode have to be considered, which is not accounted for in the absorption data shown in Figure 2a. This effect will be even more pronounced at longer wavelengths, where the overall absorption of the sensitized films is low and the absorption of back reflected light makes an important contribution to the measured IPCE value. Taking this reflection into account by basic modeling, we can roughly estimate that for the N719 device around 70 % of the absorbed photons is finally converted to current at the peak wavelength at 510 nm. This value is higher than the 60 % conversion for the D102 device, which indicates that the high performance of the device is mainly due to the high absorption coefficient of the organic dye, whereas the conversion of absorbed photon to current is higher in the N719 device. In general we can state that organic sensitizers have a great potential for their application in solid state dye sensitized solar cells due to their high absorption coefficients compared to ruthenium sensitizers. The optimal TiO_2 film thickness of such devices is generally on the order of only a few micrometers, where the use of organic dyes with high extinction coefficient generally has a stronger impact than for conventional electrochemical solar cells with film thicknesses of about 10 µm.

Figure 2b shows the current voltage characteristics for our solar cell under different illumination intensities. The D102 sensitized cells show a high open circuit voltage of V_{oc} > 850 mV, which is higher than the values for ruthenium dyes, which is around ~750 mV, when no additives are present in the dye solution. The short circuit current goes up to I_{sc} > 7.5 mA/cm^2 and the filling factor of these cells is FF ~ 60 %. This leads to an overall efficiency of η = 4.1 %. Even though no further optimization has been done yet, this value is already extraordinarily high and exceeds the former reported value of 3.2 % for a cell with a ruthenium dye as sensitizer,

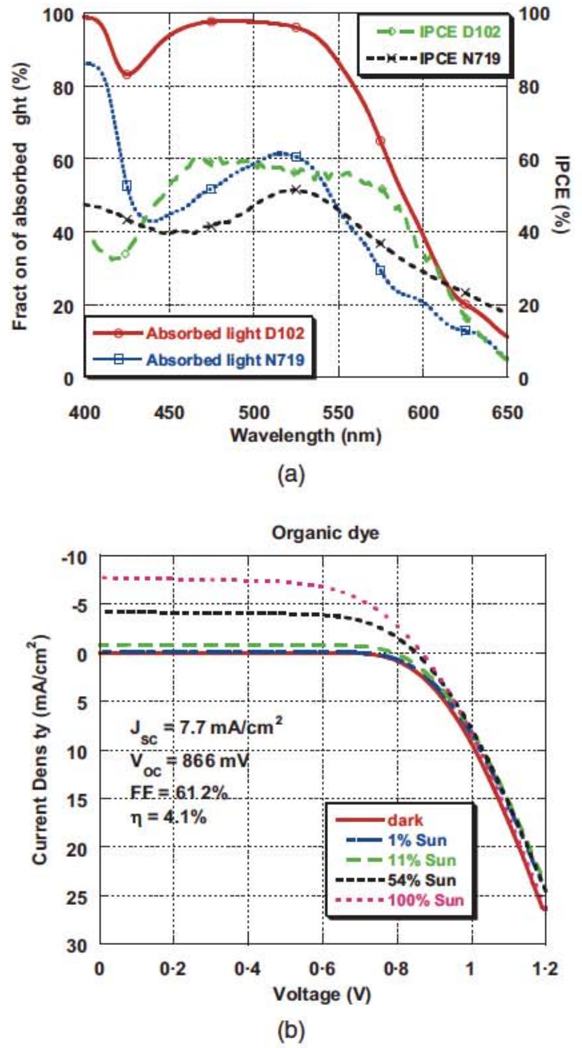

Figure 2. a) Fraction of absorbed light in the dyed TiO_2 layer (doped with either D102 or N719), prior to the evaporation of the top gold electrode, and IPCE spectrum of the complete devices. The thickness of the D102 sample is 1.6 μm and of the N719 sample 2.0 μm, which correspond to the ideal thickness of the particular device. b) Current voltage characteristics of the indoline dyed devices (device size: 0.152 cm^2, 1.6 μm thick nanoporous TiO_2 layer, 1 h dye uptake time).

which was achieved only after several years of optimization. Very recently we achieved a device performance of 4 % with a new amphiphilic dye.[12] The D102 device shows an almost linear behavior under different illuminations ranging from 1 % Sun to 100 % Sun (Fig. 2b). For 11 % and 54 % Sun the efficiency is 4.4 % and this decreases only slightly to 4.1 % for 100 % Sun.

In conclusion, for the first time a metal free organic dye has shown an exceptional performance as a sensitizer for solid state dye sensitized solar cells. Devices sensitized with this dye show record efficiencies over 4 % for solid state dye sensitized solar cells. Therefore the indoline dye is the first organic dye that is a real alternative to previously used ruthenium dyes. The higher extinction coefficient makes it an ideal dye for solid state dye sensitized solar cells. This dye shows light harvesting properties superior to those of ruthenium dyes such as N719 when applied as a sensitizer of mesoporous TiO_2 layers. Furthermore, the simple and cheap synthesis makes this dye extremely interesting for industrial production. Improvement of the performance can be expected if it proves possible to engineer a dye that has a similarly high absorption coefficient but a higher conversion efficiency of photons to current, as we find in the case of the dye N719, for example.

Experimental

After cleaning (with acetone, methanol, and Helmanex (a detergent)) of fluorine doped SnO_2 glass substrates, a ~100 nm compact layer of TiO_2 was deposited by spray pyrolysis. A nanoporous layer with 18 nm TiO_2 particles was fabricated by doctor blading, followed by sintering at 450 °C. A 0.02 M aqueous $TiCl_4$ solution was deposited overnight on the TiO_2 films, after which the substrates were rinsed in water. Prior to the dye uptake the substrates were annealed at 450 °C for 10 min and then cooled to ~80 °C before being put into the dye solution. After soaking in the dye solution the substrates were rinsed in acetonitrile and the hole conductor matrix was spin coated on top of them. To finish the device production the devices were dried in an argon flow and vacuum and a 30 nm gold electrode was evaporated on top. The device size varied between 0.1 and 0.2 cm^2 with an average size of 0.16 cm^2. The devices were tested in ambient atmosphere with a 1000 W Oriel solar simulator and an AM 1.5 global filter set. The light intensity for 100 % Sun was calibrated to 100 mW/cm^2. Different filters were used to get 1 %, 10 %, and 50 % light intensity. All production steps and measurements were performed in ambient atmosphere. The devices were not sealed or otherwise protected.

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[1] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
[2] M. Grätzel, *J. Photochem. Photobiol. C* **2003**, *4*, 145.
[3] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* **1998**, *395*, 583.
[4] S. Ferrere, A. Zaben, B. A. Gregg, *J. Phys. Chem. B* **1997**, *101*, 4490.
[5] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, *Chem. Commun.* **2001**, 569.
[6] H. Tokuhisa, P. T. Hammond, *Adv. Funct. Mater.* **2003**, *13*, 831.
[7] K. Sayama, K. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakwa, *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 47.
[8] J. Krüger, R. Plass, M. Grätzel, H. J. Matthieu, *Appl. Phys. Lett.* **2002**, *81*, 367.
[9] T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* **2003**, *24*, 3036.
[10] T. Horiuchi, H. Miura, S. Uchida, *J. Photochem. Photobiol. A* **2004**, *164*, 29.
[11] J. Krüger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel, U. Bach, *Appl. Phys. Lett.* **2001**, *79*, 2085.
[12] L. Schmidt Mende, S. M. Zakeeruddin, M. Grätzel, *Appl. Phys. Lett.* **2005**, *86*, 13 504.