Chem. Mater. **2007,** *19,* 2071−2078

Photovoltaic and Interfacial Properties of Heterojunctions Containing Dye-Sensitized Dense TiO_2 and Tri-arylamine Derivatives

Erik M. J. Johansson, Patrik G. Karlsson, Maria Hedlund, Declan Ryan, Hans Siegbahn, and Håkan Rensmo*

Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

Received October 19, 2006. Revised Manuscript Received December 21, 2006

A series of solid-state heterojunctions comprising a dense TiO_2 film electrode as an electron conductor, a ruthenium polypyridine complex ($Ru(dcbpy)_2(NCS)_2$) as a light-absorbing dye, and different triarylamine derivatives as hole conductors were prepared, and their photovoltaic properties as well as the molecular and electronic interfacial structures were investigated. The photovoltaic properties were compared to systems containing the hole conductors dissolved in an organic solvent as well as to a system containing a liquid electrolyte containing the iodide/tri-iodide redox couple. Two of the solid-state heterojunctions showed conversion efficiencies close to those of the system containing the iodide/tri-iodide redox couple, while one system was clearly less efficient. To explain the differences in photovoltaic properties the electronic and molecular interfacial structures of the solid-state heterojunctions were investigated by photoelectron spectroscopy (PES). By valence level PES the electronic energy levels highest in energy for the dye and the hole conductors were mapped, and the differences in energy matching partly explain the trends in photovoltaic properties. Differences in the molecular surface structure of the heterojunctions were also observed from the N 1s core level measurements. Specifically it was found that the smaller hole conductor, showing low photocurrent yield, is inserted into the dye layer.

Introduction

Nanostructured dye-sensitized solar cells (DSSC) show promise as a low-cost alternative to conventional solid-state solar cells.[1] Many DSSC systems contain a liquid electrolyte, but replacing the liquid electrolyte with a solid hole-conducting material is possible and may give practical advantages.[2] The efficiencies of the solid-state DSSC are, however, not as high as the efficiencies obtained for systems with the liquid electrolyte containing the tri-iodide/iodide redox couple. Nonporous TiO_2 has been used in model systems containing dye and conducting polymers.[3−9] For example, Smestad et al.[5] made photoelectrochemical comparisons between nonporous dye-sensitized TiO_2 electrodes combined with polythiophenes, which showed promising quantum efficiencies. Previously, studies have also been made using triarylamine derivatives in a solid-state DSSC,[2,10−14] and the most efficient devices have energy conversion efficiencies of about 4%.[12−14]

The solid-state DSSC differ from conventional solar cells in that they more clearly separate the function of light absorption from the conduction of electrons. After the light absorption by the dye molecule, the electron is efficiently transferred into the TiO_2.[15−18] The dye is then regenerated through an electron transfer from a hole-conducting material. As a result of the effective injection process, the final efficiency is largely affected by the recombination processes of the electrons from TiO_2 to the dye or to the hole conductor and how the rates of these processes compare to the rate of the electron transfer from the hole conductor to the dye (regeneration of the dye). The transfer rates are closely

---

* Corresponding author. Phone: +46-18-4713547. Fax: +46-18-471 3524. E-mail: hakan.rensmo@fysik.uu.se.

(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(2) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583−585.
(3) Saito, Y.; Kitamura, T.; Wada, Y.; Yanagida, S. *Synth. Met.* **2002**, *131*, 185−187.
(4) Saito, Y.; Fukuri, N.; Senadeera, R.; Kitamura, T.; Wada, Y.; Yanagida, S. *Electrochem. Commun.* **2004**, *6*, 71.
(5) Smestad, G. P.; Spiekermann, S.; Kowalik, J.; Grant, C. D.; Schwartzberg, A. M.; Zhang, J.; Tolbert, L. M.; Moons, E. *Sol. Energy Mater. Sol. Cells* **2003**, *76*, 85.
(6) Grant, C. D.; Schwartzberg, A. M.; Smestad, G. P.; Kowalik, J.; Tolbert, L. M.; Zhang, J. Z. *Synth. Met.* **2003**, *132*, 197.
(7) Spiekermann, S.; Smestad, G.; Kowalik, J.; Tolbert, L. M.; Grätzel, M. *Synth. Met.* **2001**, *121*, 1603.
(8) Liu, Y.; Summers, M. A.; Edder, C.; Frechet, J. M. J.; McGehee, M. D. *Adv. Mater.* **2005**, *17*, 2960.
(9) Johansson, E. M. J.; Sandell, A.; Siegbahn, H.; Rensmo, H.; Mahrov, B.; Boschloo, G.; Figgemeier, E.; Hagfeldt, A.; Jönsson, S. K. M.; Fahlman, M. *Synth. Met.* **2005**, *149*, 157.
(10) Hagen, J.; Schaffrath, W.; Otschik, P.; Fink, R.; Bacher, A.; Schmidt, H. W.; Haarer, D. *Synth. Met.* **1997**, *89*, 215−220.
(11) Jäger, C.; Haarer, D.; Peng, B.; Thelakkat, M. *Appl. Phys. Lett.* **2004**, *85*, 6185.
(12) Schmidt-Mende, L.; Bach, U.; Humphry-Baker, R.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2005**, *17*, 813.
(13) Snaith, H. J.; Zakeeruddin, S. M.; Schmidt-Mende, L.; Klein, C.; Grätzel, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6413.
(14) Schmidt-Mende, L.; Zakeeruddin, S. M.; Grätzel, M. *Appl. Phys. Lett.* **2005**, *86*, 013504.
(15) Eichberger, R.; Willig, F. *Chem. Phys.* **1990**, *141*, 159.
(16) Tachibana, Y.; Moser, J. E.; Gratzel, M.; Klog, D. R.; Durrant, J. R. *J. Phys. Chem.* **1996**, *100*, 20056.
(17) Benkö, G.; Myllyperkiö, P.; Pan, J.; Yartsev, A. P.; Sundström, V. *J. Am. Chem. Soc.* **2003**, *125*, 1118−1119.
(18) Schnadt, J.; Bruhwiler, P. A.; Pattey, L.; O'Shea, J. N.; Södergren, S.; Odelius, M.; Ahuja, R.; Karis, O.; Bässler, M.; Persson, P.; Siegbahn, H.; Lunell, S.; Mårtensson, N. *Nature* **2002**, *418*, 620−623.

10.1021/cm062498v CCC: $37.00

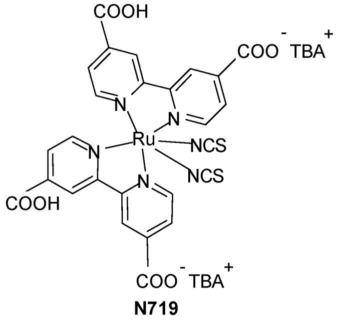

Figure 1. Molecular structure of the dye N719 used in the present study.

connected to the energy-level matching between the materials at the interface as well as their combined geometrical structure. Previously, it has been shown that the choice of the dye molecule affects the photovoltage in a solid-state heterojunction.[9] Particularly the size of the dye has also been shown to affect the photovoltage.[19] These examples show that the interfacial molecular structure and the energy-level matching are important for the transfer rates at the interface.

Insight into the molecular electronic structures of the interface between the semiconductor, dye, and hole-conductor molecules is therefore useful in understanding the properties of the heterojunction, and such information can be obtained by photoelectron spectroscopy (PES) measurements as has been shown previously.[9,20−25] Specifically, it was concluded that the interactions and the individual properties of the different materials at the interfaces play an important role for the properties of the heterojunctions.[9,24]

In this study we investigate heterojunctions that are model systems for DSSC and that contain hole-conducting triarylamine derivative molecules. The system consists of a nonporous ("dense") TiO_2 electron conducting material, a ruthenium−polypyridine dye complex ($Ru(dcbpy)_2(NCS)_2$, N719) as a light absorbing material, and triarylamine derivative molecules as the organic hole-conducting material, see Figures 1 and 2. The triarylamine derivatives used have only a minor light absorption in the visible region and are therefore candidates also in nanostructured systems. They were used either in the solid state or as part of a liquid electrolyte, which makes it possible to make a comparison between a solid state and liquid (solvated) state heterojunction using the same hole-conducting molecule. Some of the prepared model systems were shown to have photovoltaic properties comparable to a system with a liquid electrolyte containing the iodide/tri-iodide redox couple while some of the solid heterojunctions were clearly less efficient.

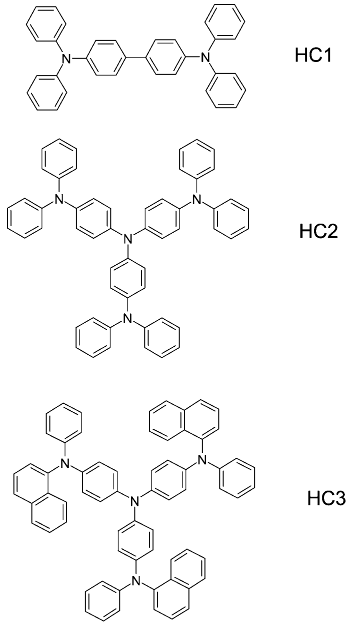

Figure 2. Molecular structures of the hole-conductor molecules.

A specific objective with the present investigation is to show how to prepare relevant interfaces to be able to map the electronic and molecular structures of complete TiO_2/dye/hole-conductor heterojunctions by PES and thereby partly explain some of the differences observed in the photovoltaic properties of a series of systems.

Experimental Section

The nonporous TiO_2 layer was made by spray pyrolysis[26] on conducting glass (SnO_2:F on glass). The synthetic procedure differs from that in ref 26 only in that N_2 was used instead of pressurized air to spray the solution. The thickness of the layers was in the order of 100 nm as measured by a Dektak3 surface profile meter. The dye $Ru(dcbpy)_2(NCS)_2$ (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium) was purchased from Solaronix S.A., and the dye solution was 0.5 mM in ethanol. The samples were sensitized for 1 h in the dye solution.

The hole-conductor molecules (see Figure 2) were purchased from Sensient Imaging Technologies GmbH. The solid-state heterojunctions for the photovoltaic measurements were made by vacuum deposition of the hole conductor and a gold layer onto a dye-sensitized TiO_2 film, see schematic picture in Figure 3. The deposition was performed in a chamber with a base pressure of about 10^{-8} Torr. The hole-conductor material was put into a glass tube containing a millimeter large nozzle and was then deposited using resistive heating from a tungsten wire winded around the tube. Finally, a contact to the heterojunction was made in the same chamber by depositing a gold layer onto the hole-conductor layer. Initially photovoltages and photocurrents of the system grew with time and stabilized after a few hours of illumination (100 mW/cm^2). At the same time the resistance over the heterojunction grew. Electrical shorting of thin organic solar cells is common and may arise from metal migration of small amounts of Au into the organic thin films during the vacuum deposition. In fact, transmission electron microscopy (TEM) experiments indicate that small amounts

---

(19) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Gratzel, M. *Nano Lett.* **2005**, *5* (7), 1315−1320.
(20) Westermark, K.; Rensmo, H.; Siegbahn, H.; Keis, K.; Hagfeldt, A.; Ojamae, L.; Persson, P. *J. Phys. Chem. B* **2002**, *106*, 10102.
(21) Rensmo, H.; Westermark, K.; Södergren, S.; Kohle, O.; Persson, P.; Lunell, S.; Siegbahn, H. *J. Chem. Phys.* **1999**, *111*, 2744−2750.
(22) Westermark, K.; Rensmo, H.; Schnadt, J.; Persson, P.; Södergren, S.; Brühwiler, P. A.; Lunell, S.; Siegbahn, H. *J. Chem. Phys.* **2002**, *285*, 167.
(23) Johansson, E. M. J.; Hedlund, M.; Siegbahn, H.; Rensmo, H. *J. Phys. Chem. B* **2005**, *109* (47), 22256−22263.
(24) Karlsson, P. G.; Bolik, S.; Richter, J. H.; Mahrov, B.; Johansson, E. M. J.; Blomquist, J.; Uvdal, P.; Rensmo, H.; Siegbahn, H.; Sandell, A. *J. Chem. Phys.* **2004**, *120* (23), 11224−11232.
(25) Mahrov, B.; Boschloo, G.; Hagfeldt, A.; Siegbahn, H.; Rensmo, H. *J. Phys. Chem. B* **2004**, *108*, 11604−11610.
(26) Kavan, L.; Grätzel, M. *Electrochim. Acta* **1995**, *40*, 643−652.

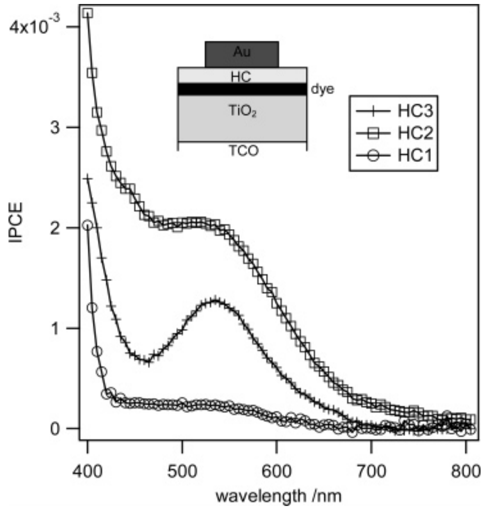

Figure 3. IPCE spectra for the solid-state systems. Inset: Schematic picture of the solid-state devices.

of metal penetrate more than 100 nm into the organic film during vacuum deposition.[27] However, the increase in resistance indicates that illumination of the heterojunction removes this shortening. The reason of the increased efficiency after illumination is however not the subject of the present report, which instead focuses on the properties of the stabilized systems.

The junctions containing dissolved hole conductors (liquid based hole-conductor heterojunctions) were made by placing a spacer (wipes, Kimberly-Clark, Kimwipes Lite) between the dye-sensitized TiO_2 and a conducting glass plate, and then a solution of the hole conductor (3 mM) dissolved in dichloromethane and propylene carbonate (4:1) was added dropwise on the spacer. Partial oxidation of the hole conductors was made by adding $N(PhBr)_3SbCl_6$ to the hole-conductor solution in a number of different concentrations ranging from 0.3 mM to 1.5 mM. The heterojunction with tri-iodide/iodide electrolyte was made similar to the liquid based hole-conductor heterojunctions; the back contact was a platinized conducting glass. The tri-iodide/iodide electrolyte contained 0.5 M LiI and 0.05 M I_2 in propylene carbonate.

The incident photon to current conversion efficiencies (IPCEs) were measured for the systems over an interval of wavelengths. These measurements were obtained with a Keithley 6487 Sourcemeter, a Spectral Products CM110 monochromator, and a General Electric ELH 300 W lamp. The calibration was made using a Si photodiode (Hamamatsu S1337-33BR). The current versus voltage (*IV*) measurements were made using a xenon lamp (Osram 250W) and a Keithley 6487 Sourcemeter. The intensity was calibrated using a Newport 818-UV photodetector. The software for the IPCE and the *IV* setup was made by Solarena AB. The long-term stability tests were performed for 1 week using a tungsten−halogen light source (Spectral Products) equipped with a UV filter. On the basis of the integrated photocurrent and by estimating the amount of dye molecules from the IPCE (assuming 100% quantum efficiency) this illumination (10 mW/cm^2) was equivalent to several thousands of turnovers.

Samples for the PES measurements were produced by depositing the hole conductor at the dye-sensitized TiO_2 surface by resistive heating as described above. The thickness of the resulting hole-conductor layer varied with the distance from the glass nozzle. In these investigations the thickness of the hole-conductor layer was limited to a few monolayers to facilitate the characterization of the interface between the dye-sensitized dense TiO_2 and the hole-conducting molecules. A mask was shielding part of the dye-sensitized substrates to facilitate a comparison to a sample of dye-sensitized TiO_2 without any hole-conductor molecules.

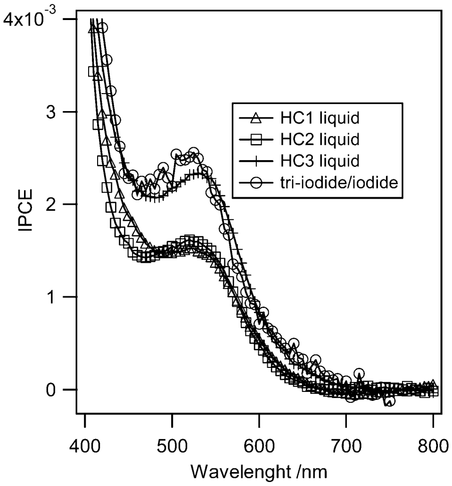

Figure 4. IPCE spectra for the liquid based systems.

The PES measurements were performed using synchrotron light at BL I411 at the Swedish national laboratory MAX in Lund.[28] The takeoff angle (θ) used was 80°, and the angle between polarization and photoelectron direction was 0°. The spectra were energy calibrated to the dye-sensitized substrate the same way as reported in ref 23. The N 1s spectra of the dye-sensitized TiO_2 and the dye-sensitized TiO_2 with a thin hole-conductor layer were intensity normalized to Ti 2p. The valence spectra were measured at the same light intensity and were consequently only intensity normalized by acquisition time. From the intensity drop of the Ti 3p peak upon evaporation of the hole conductor, the thickness of the hole-conductor layer was estimated. Samples referred to as having a *thin* layer of hole conductors deposited contain an amount that is about half a monolayer while samples referred to as having a *thick* layer deposited contain amounts clearly above a monolayer.

Results and Discussion

Incident Photon to Current Conversion Efficiency. The IPCEs were measured for a number of systems. Figure 3 shows the IPCE measurements of the solid-state systems containing TiO_2, N719, and the different hole conductors. All three systems show the photoresponse in the region expected from the absorption properties of the dye (peak maxima at about 530 nm). Although the peak values differ slightly, which may indicate some specific interaction between the different hole conductors and the dye molecule, this shows that the dye absorbs light and injects electrons to the TiO_2 and that the hole conductor transfers electrons to the dye molecule. If we compare the efficiencies of the different systems in the visible region we observe that the TiO_2/N719/HC2 heterojunction shows the highest efficiency, the TiO_2/N719/HC3 heterojunction shows a somewhat lower

---

[27] Suemori, K.; Miyata, T.; Yokoyama, M.; Hiramoto, M. *Appl. Phys. Lett.* **2004**, *85*, 6269−6271.

[28] (a) Svensson, S.; Forsell, J.-O.; Siegbahn, H.; Ausmees, A.; Bray, G.; Södergren, S.; Sundin, S.; Osborne, S. J.; Aksela, S.; Nömmiste, E.; Jauhiainen, J.; Karvonen, M. J.; Salaneck P. W. R.; Evaldsson, A.; Lögdlund, M.; Fahlman, A. *Rev. Sci. Instrum.* **1996**, *67*, 2149. (b) Bässler, M.; Forsell, J.-O.; Björneholm, O.; Feifel, R.; Jurvansuu, M.; Aksela, S.; Sundin, S.; Sorensen, S. L.; Nyholm, R.; Ausmees, A.; Svensson, S. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101*−*103*, 953.

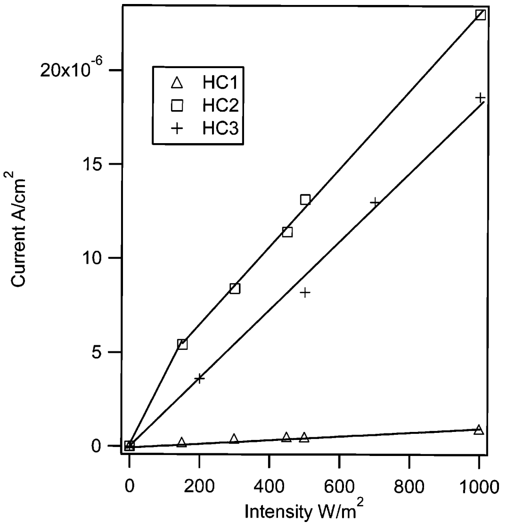

Figure 5. Short-circuit current versus intensity for the solid-state heterojunctions.

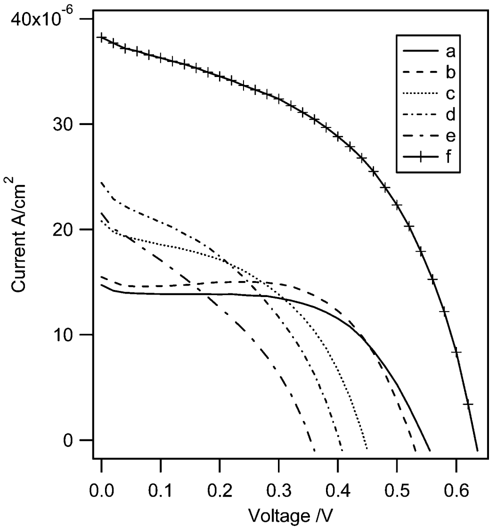

Figure 6. Current vs voltage measurements of liquid based systems. (a) HC3 without oxidation agents, (b) 3 mM HC3 and 0.3 mM $N(PhBr)_3SbCl_6$, (c) 3 mM HC3 and 0.6 mM $N(PhBr)_3SbCl_6$, (d) 3 mM HC3 and 0.9 mM $N(PhBr)_3SbCl_6$, (e) 3 mM HC3 and 1.5 mM $N(PhBr)_3SbCl_6$, and (f) iodide/tri-iodide redox couple; see Experimental Section.

efficiency, and the efficiency of the TiO_2/N719/HC1 system is clearly lower. We also note that the heterojunctions show IPCE values higher than expected for a system based on a perfectly flat oxide surface. Although the films studied here are dense,[26] they are not perfectly flat, which is a reasonable explanation for these rather high photoconversion efficiencies.

The present report is not foucused on the long-term stability of the devices, but some preliminary tests have been performed for the most efficient system. The photocurrent yield was stable during one week of white light illumination, and during this time no spectral changes were observed in the IPCE spectrum indicating good stability of the dye molecule in the present configuration. Moreover, for a device stored in the dark for more than half a year the IPCE value has only decreased by 20%.

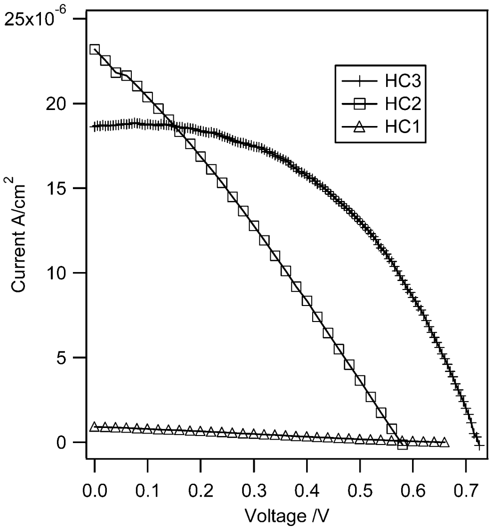

Figure 7. Current vs voltage characteristics of the solid-state systems.

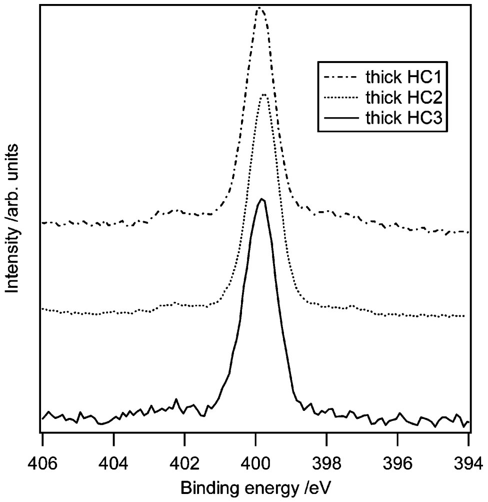

Figure 8. N 1s core level structure of multilayers of HC1, HC2, and HC3 on dye-sensitized TiO_2 (measured with a photon energy of 758 eV).

Table 1. Open-Circuit Voltages of Systems with Solid-State Hole Conductors and Systems with the Hole Conductors Dissolved (3 mM) in Dichloromethane and Propylene Carbonate (4:1)

	open-circuit voltage (V)		
system	system with HC1	system with HC2	system with HC3
solid-state HC	0.66	0.58	0.73
dissolved HC	0.57	0.34	0.54

Figure 4 shows the results from IPCE measurements on liquid based systems containing the different hole conductors as well as a system containing the iodide/tri-iodide redox couple. In comparison with the iodide/tri-iodide electrolyte based system, the hole-conductor based systems give somewhat lower IPCE, except for the system based on HC3, which gives similar photoresponse. This comparison, with an electrolyte known to be very efficient, shows that the hole conductors under certain conditions efficiently transfer electrons to the dye during operation.

Finally we compare the results from the solid heterojunctions with those of the liquid based systems. We note that it was possible to build a configuration (TiO_2/N719/HC2) showing IPCE properties almost similar to those of the most efficient liquid based systems. Second, trends in the efficiencies obtained from the different hole conductors are different in the liquid based systems and in the solid systems. Third, we note that the IPCE for the liquid

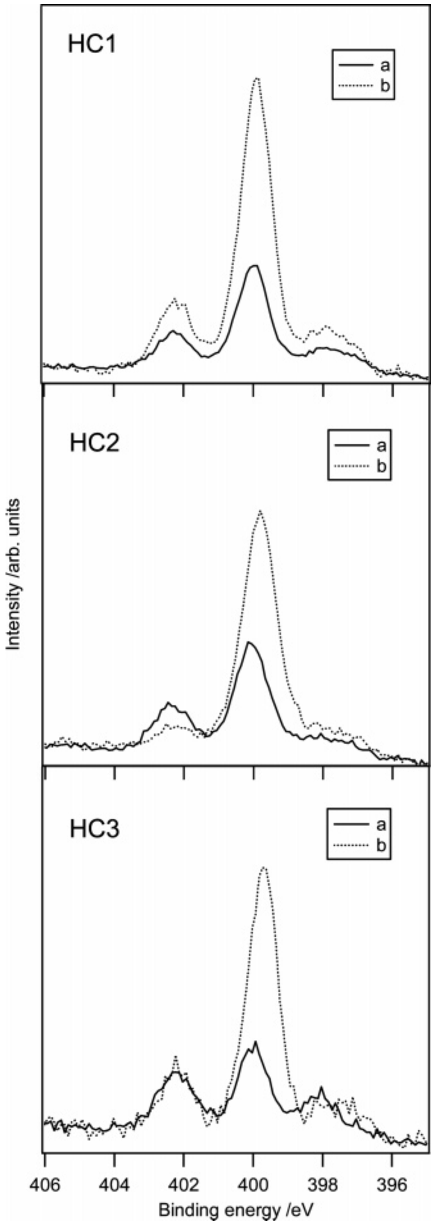

Figure 9. Top: N 1s core level structure of (a) dye-sensitized TiO_2 and (b) dye-sensitized TiO_2 with a thin layer of HC1. Middle: N 1s core level structure of (a) dye-sensitized TiO_2 and (b) dye-sensitized TiO_2 with a thin layer of HC2. Bottom: N 1s core level structure of (a) dye-sensitized TiO_2 and (b) dye-sensitized TiO_2 with a thin layer of HC3. All spectra were measured with a photon energy of 758 eV.

systems are rather similar while they vary substantially for the solid based systems.

The IPCE is largely dependent on the difference in the electron-transfer rate from the hole conductor to the dye after the injection (regeneration of the dye) compared to the recombination of electrons from TiO_2 to the dye or to the hole conductor. These electron-transfer rates are dependent on the geometry of the interface and the energy-level matching between the different materials. To understand the variations in IPCE for the systems, there is therefore a need to understand the geometry and the electronic structure of the interfaces in the systems. In the PES section below the geometrical and electronic differences of the solid-state systems are investigated. However, before the PES measurements are discussed we report on the total photocurrent and photovoltage characteristics during light illumination.

Photocurrent and Photovoltage Measurements During White Light Illumination. The short-circuit current during white light illumination was measured at a number of different light intensities for the different solid-state systems, and the results are shown in Figure 5. From the figure we observe that the trend in conversion efficiency observed in the IPCE measurements is preserved also at higher light intensities, that is, the system based on HC2 is most efficient, and the system based on HC1 is less efficient. Interestingly, the currents are almost proportional to the light intensities all the way up to an intensity of 1000 W/m^2, indicating that the charge transfer between the hole conductor and the dye also can be efficient at high light intensities. A slight deviation from this behavior is observed for HC2 at lower light intensities.

Before discussing the photovoltage properties for the solid-state systems, the photovoltage properties of a liquid based system containing a hole conductor are reported. Figure 6 shows an example of the *IV* measurements of the liquid based system containing HC3 and different concentrations of the molecule $N(PhBr)_3SbCl_6$. This molecule efficiently oxidizes the hole conductor defining the redox potential in the electrolyte. Upon increasing the amount of oxidized molecules, the short-circuit current increases. In these measurements the currents are generally 2−3 orders of magnitude higher than when performing the IPCE measurements emphasizing also the importance of reactions at the counter electrode. The increase observed in short-circuit current when adding small amounts of the oxidizing molecule $N(PhBr)_3SbCl_6$ may therefore be expected from the higher probability to transfer electrons from the counter electrode to the electrolyte. More important for the discussion below and contrary to the trend for short-circuit current, the open-circuit voltage decreases with increasing concentration of the oxidized hole conductor. This decrease in open-circuit voltage is probably an effect from increased recombination rate at the dye-sensitized surface when increasing the amount of electron scavengers (oxidized hole-conductor molecules). Also the general changes in shape of the $I-V$ curve, observed as a decrease in shunt resistance and fill factor, may partly be explained by such an increase in recombination rate at the dye-sensitized surface.

The *IV* characteristics of the solid-state systems are shown in Figure 7. All systems show photovoltaic properties, and the results differ for the systems based on different hole conductors. The open-circuit voltages of the solid-state systems in Figure 7 are first compared to the open-circuit voltages of liquid based systems with the hole conductors, and because the amount of oxidized hole-conductor molecules is expected to be very small in the solid heterojunctions, we compared the results from the solid systems with those of the liquid systems containing no $N(PhBr)_3SbCl_6$. The open-circuit voltages of the liquid and solid systems were found to differ substantially; see Table 1. All systems show higher photovoltages in the solid-state systems compared to the liquid based systems. HC1 shows about 0.1 V higher open-circuit voltage and HC2 and HC3 show about 0.2 V higher open-circuit photovoltage in the solid-state system. The maximum open-circuit voltage in a liquid based system

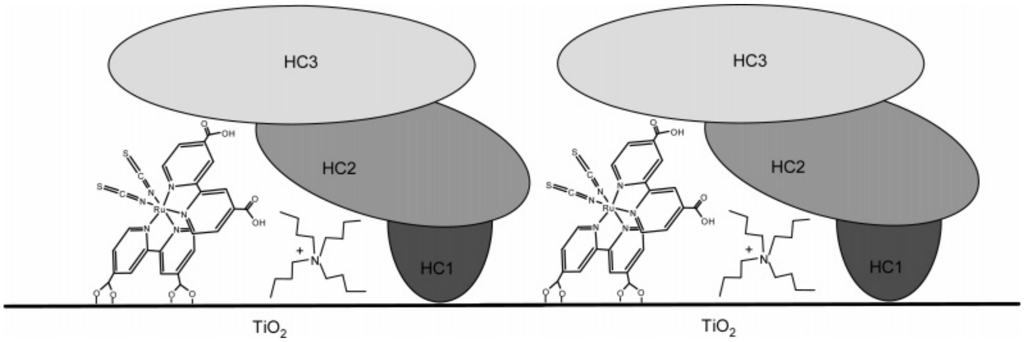

Figure 10. Schematic figure highlighting the position of the different hole conductors in the molecular interface structures. Specifically the figure shows that the smaller hole conductor (HC1), showing low photocurrents, is inserted into the dye layer while the larger hole-conductor (HC3), showing higher photocurrents, is not inserted into the dye layer.

is often approximated to the difference between the conduction band edge of TiO_2 and the redox potential of the redox couple in the electrolyte. This model gives reasonable agreement for the systems containing the iodide/tri-iodide redox couple.[29] Similarly to the liquid based systems, the predicted photovoltages in solid-state systems are often approximated by the difference between the conduction-band edge of TiO_2 and the oxidation redox potential of hole conductor. If we adopt this approach for the systems studied here, the system with HC1 should have the highest open-circuit voltage and HC2 and HC3 should have about 0.5 V lower open-circuit voltage than HC1.[30] Moreover, the open-circuit voltage of the liquid system with HC3 should, based on the same approximation, be higher than that containing the iodide/tri-iodide redox couple, since the redox-potential for HC3/$HC3^+$ is higher than for tri-iodide/iodide.[30] However, the experimental results differ from the expectations from the models. It is obvious that also other parameters such as the geometry and the electronic structure of the interfaces affect the photovoltage in the systems studied here. The PES results reported below help us to understand these differences.

Finally, we note that the general shape of the *IV* curves differ substantially when comparing the solid-state systems. There are several explanations for such changes including different charge transport properties within the different materials and differences in shunt resistance. With respect to these factors the present investigating will shed some light on the latter in terms of a better understanding of the TiO_2/dye/hole-conductor interface.

PES Measurements. The N 1s core level spectra of multilayers of the hole conductors on dye-sensitized TiO_2 are shown in Figure 8. The N 1s contribution corresponding to the hole conductors is clearly observed as a single peak. Because no other contributions are observed in the spectra of the hole conductors, the amounts of oxidized hole-conductor molecules have to be very small in these solid-state films. We also note that the peak position is very similar (shifted less than 0.4 eV) in comparison with the N 1s peak originating from the bi-pyridine ligand of the dye;[23] see below.

Figure 9 shows the N 1s core-level spectra for dye-sensitized TiO_2 and dye-sensitized TiO_2 covered with thin layers of evaporated HC1, HC2, and HC3. All spectra were normalized with respect to a substrate signal (Ti 2p).

In the spectra without hole-conductor contributions we observe three different peaks originating from the dye molecule. Starting at high binding energy, the peaks have previously been assigned to nitrogen in the tetrabutylammonium (TBA+) counterion, nitrogen in the bipyridine ligands, and the nitrogen in the NCS units.[23] In comparison with spectrum from a dye-sensitized nanostructured TiO_2, the TBA peak is more intense, and the NCS peak is clearly broader for the dye-sensitized dense TiO_2 film studied here.[23] This indicates that the surface structure of the dense TiO_2 differs somewhat from that of the nanostructured TiO_2.

Now turning to the spectra measured for thin layers of hole conductor deposited on the dye-sensitized TiO_2 surface which are also shown in Figure 9 (dots). By following the observed changes in intensity in peaks originating from the dye (i.e., NCS at 397.5 eV) and the counterion (i.e., TBA+ at 402.2 eV) relative the substrate signal we can understand where the molecules adsorb to the surface. In the case of HC1 (Figure 9), the intensity of the peaks corresponding to the dye, and the counterion is higher in the spectrum with hole conductor compared to the spectrum without the hole conductor (about 60% and 80%, respectively). Therefore, assuming very similar mean free path for electrons emitted from the substrate (Ti 2p) and the dye (N 1s) at this particular photon energy, this decrease in the substrate (TiO_2) signal relative the N 1s signal, from the TBA and NCS units originating from the dye, indicates that the HC1 molecules selectively are placed beside the dye and the TBA molecules at the TiO_2 surface or, in other words, are inserted into the dye layer; see Figure 10.

In the case of HC2 (Figure 9) the peak intensity corresponding to the dye (NCS) increases about 10% when adsorbing a thin layer of hole conductor. Again this indicates that some of the HC2 molecules are placed between the dye molecules. In the case of HC2, however, the TBA signal intensity decreases about 30% indicating that a fraction of the molecules in this thin layer also selectively adsorbs on the TBA+ ions; see Figure 10.

Interestingly, in the case of HC3 (Figure 9), the intensity of the peaks corresponding to the dye and TBA is rather constant, that is, the adsorption of the HC3 molecule at the interface dampens the signals from the dye and TBA with the same magnitude as it dampens the signals from the TiO_2

---

(29) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49−68.
(30) http://www.hwsands.com.

substrate. These results therefore indicate that the HC3 molecules are randomly placed over the surface and are not inserted into the dye layer; see Figure 10. In this context it is interesting to note that HC3 is the largest molecule while HC1 is the smallest one. A shift of the NCS signal is also observed, indicating an interaction between the dye and HC3. Shifts of the N 1s feature corresponding to NCS have been observed before for dye molecules interacting with CuI[24,25] as well as ZnO.[20]

Generally, the geometrical position of the hole-conductor molecules at the interface affects the recombination rate from the TiO_2 to the hole conductor. The variations in the position of the hole conductors discussed above may therefore partly explain the differences observed in the photoconversion properties measured for the solid-state systems. For example, the unfavorable position of the HC1 and partly also the HC2 molecules between the dye molecules on the TiO_2 substrate can affect the charge recombination rate and thereby the shorts circuit current (HC1) and the fill factor (HC2). The favorable molecular interface in the system containing HC3 partly explains the superior performance of this heterojunction.

The electronic structures of the outermost energy levels are also important in the photoinduced charge-transfer reactions at the dye interface. These electron-transfer rates depend partly on the energy-level matching between the highest occupied molecular orbital (HOMO) level of the hole conductor and the dye and the matching between the conduction band of TiO_2 and the HOMO level of the hole conductor. Information on electronic matching between the different materials may be obtained from PES measurements of the valence level structure as reported below.

Different valence level spectra of dye-sensitized TiO_2 covered with an increasing amount of HC1 are shown in Figure 11a. The spectrum of the dye-sensitized TiO_2 shows the highest occupied electronic structure of the dye appearing as a peak above the valence band of TiO_2. Such spectra have been observed previously.[9,21−24] The spectra also containing contributions from HC1 deposited on the dye-sensitized film show that a peak is growing at a binding energy slightly higher than the structure observed for the dye.

The valence structure of the dye-sensitized TiO_2 together with the spectra of an interface containing an increasing amount of HC2 contribution is shown in Figure 11b. The spectra of the interface containing HC2 show a peak at a binding energy very similar to that observed for HC1. However, the contribution from HC2 also contains a knee at lower binding energies (shifted about 0.5 eV). The appearance of this new structure at lower binding energy agrees with the shift in redox potential comparing HC2 and HC1.[30]

The spectra of an interface containing HC3, Figure 11c, also show an extra component at lower binding energies (shifted about 0.5 eV). The extra component is close in binding energy to that observed for HC2, which agrees with the similarity in redox potential for HC3 compared to HC2 (0.36 V vs SCE for HC3 compared to 0.38 V vs SCE for HC2[30]).

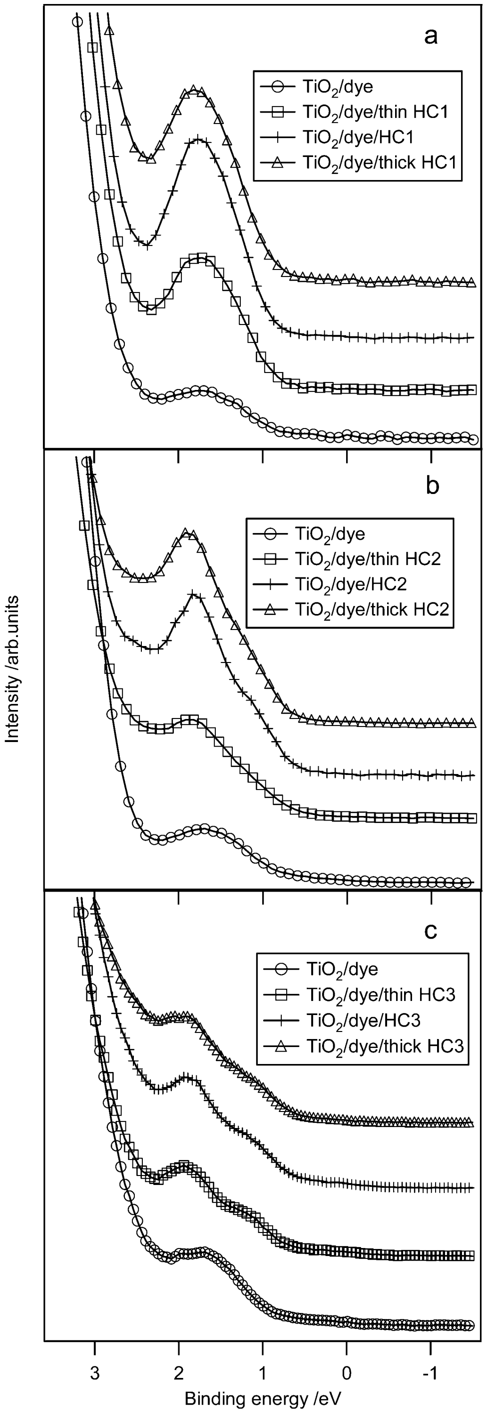

Figure 11. (a) Valence electronic structure of dye-sensitized TiO_2 and dye-sensitized TiO_2 with HC1 (measured with a photon energy of 110 eV). (b) Valence electronic structure of dye-sensitized TiO_2 and dye-sensitized TiO_2 with HC2 (measured with a photon energy of 160 eV). (c) Valence electronic structure of dye-sensitized TiO_2 and dye-sensitized TiO_2 with HC3 (measured with a photon energy of 140 eV).

In a simple energy level picture of the interfaces, the HOMO of the hole conductor should have lower binding energy than the HOMO of the dye for efficient regeneration of the dye by the hole conductor to take place. The position of the highest occupied electronic structures of HC1 at a slightly higher binding energy than the occupied electronic structures of the dye may therefore explain the low short-circuit currents of the systems with HC1. The extra structure in the highest occupied molecular structure of HC2 and HC3, which has a position shifted about 0.5 eV more toward lower binding energy than the dye peak, is in favor for efficient regeneration and may be the reason for higher short-circuit currents of systems containing HC2 and HC3 compared to the system containing HC1.

Interestingly, the observed trends in photovoltage of the systems do not agree with the energy-level picture from the PES measurements, since HC1 has the highest binding energy of the highest occupied electronic structure, which then would result in the highest photovoltage. However, since the efficiency for regeneration of the dye by the hole conductor is likely to be low for the systems with HC1, the recombination reactions will lower also the photovoltage. This may therefore explain why the photovoltage for the solid system containing HC1 falls below that of HC3.

Conclusions

All TiO_2/dye/hole-conductor heterojunctions showed IPCE spectra expected from the absorption properties of the dye, which shows that the dye injects electrons into the TiO_2 layer and that the hole conductor transports electrons to the dye. Comparing a series of liquid based systems with that of a solid system, it was observed that the trends in IPCE obtained are different. We note that the efficiency for the liquid systems is rather similar while it varies substantially for the solid system. The solid-state heterojunction, containing the larger molecules, shows IPCE values comparable those of a system containing the well-known tri-iodide/iodine redox couple. This shows that the conversion process for the solid systems could be very effective. The solid-state heterojunction containing the smallest molecule (HC1) clearly showed much lower photocurrents.

Generally, the solid-state heterojunctions gave higher open-circuit voltages than the liquid based analogues. We also note that the trends observed in the photovoltages for the solid-state heterojunctions are different from what are expected for the redox potentials of the molecules.

The photoconversion properties could partly be explained by the PES characterization of the interfacial molecular and electronic structures. For example, the PES characterization for interfaces containing HC1, showing low current conversion and unexpectedly low photovoltage, indicated an interfacial molecular structure in favor of charge recombination from the TiO_2 substrate to the hole conductor and an electronic matching that is unfavorable for electron transfer from the hole conductor to the dye molecule.

In contrast, the valence level spectra of HC2 and HC3 showed an extra contribution in the valence electronic structure at lower binding energies facilitating quick regeneration of the dye after electron injection. Also the results from the N 1s core level spectra showed favorable molecular interfacial structure in the system containing the large molecule (HC3) which partly explains the superior performance of this heterojunction.

Acknowledgment. This work was supported by the Swedish Science Council (VR), the Göran Gustafsson Foundation, the Swedish Foundation for Strategic Research (SSF), and the Carl Trygger Foundation. We thank the staff at MAX-lab for competent and friendly assistance.

CM062498V