Angewandte Chemie

DOI: 10.1002/anie.200705225

Dye-Sensitized Solar Cells

Organic Dye-Sensitized Ionic Liquid Based Solar Cells: Remarkable Enhancement in Performance through Molecular Design of Indoline Sensitizers**

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Dye-sensitized solar cells (DSCs) have attracted large attention in scientific research and for practical applications owing to the potential advantages of low cost, easy production, flexibility, and transparency relative to conventional crystalline silicon solar cells.[1,2] Over the past decade, significant progress was made in terms of the performance and stability of DSC devices.[3–6] The sensitizer is a crucial element in DSCs, exerting significant influence on the power conversion efficiency as well as the stability of the devices. Although the most efficient sensitizers to date are ruthenium complexes, organic dyes have been attracting intensive research efforts because of their ease of synthesis, high molar extinction coefficient, tunable absorption spectral response from the visible to the near infrared (NIR) region, as well as environmentally friendly and inexpensive production techniques.[7–10] Recently, 9% power conversion efficiency was reported for an organic-dye-sensitized solar cell used in combination with a volatile solvent (e.g., acetonitrile) electrolyte.[7b] Owing to encapsulation and stability issues at higher temperatures, nonvolatile or ionic-liquid electrolytes are preferred over volatile analogues. Ionic liquids (ILs) in particular are very attractive because of their negligible vapor pressure under photovoltaic operating conditions as well as their high conductivity and thermal stability.[4,11–15] IL-based DSCs with ruthenium complexes as sensitizers have already shown impressive photovoltaic performance and stability.[4,11] However, their conversion efficiency still lags behind those of organic-solvent-containing DSCs. The main reason for the lower performance is the high viscosity of ILs, which produces mass-transfer limitations on the photocurrent under full sunlight. Organic sensitizers offer very attractive prospects to overcome this drawback, as their extinction coefficients in the visible are much higher than those of the ruthenium complexes employed so far. This allows light harvesting to be accomplished with thinner TiO_2 films, alleviating the mass-transport problem. Herein we report on the achievement of 7.2% solar (air mass (AM) 1.5, $100\,mW\,cm^{-2}$ irradiation) to electric power conversion efficiency using a molecularly tailored indoline sensitizer. To our knowledge this is the first time such high efficiency has been obtained for organic-dye-based DSCs employing an ionic-liquid electrolyte. Electrochemical impedance and photovoltage transient studies reveal the pivotal influence exerted by the chemical structure of the indolene dye on the photovoltaic response of the device.

The molecular structures of the three indoline-based organic dyes examined in this study are presented in Figure 1. The D149 sensitizer was obtained by attaching a second rhodanine unit to the D102[7a] structure, thus extending its π conjugation. Replacing the ethyl group on the terminal rhodanine unit of D149 by an octyl chain yields the third sensitizer in the series, coded D205. The three sensitizers were synthesized as reported earlier.[7a] The increased conjugation in D149 and D205 results in a red shift of the visible spectrum with respect to D102. Thus, the absorption maxima for D149 in the *tert*-butyl alcohol and D205 in THF are at $\lambda = 526$ nm ($\varepsilon = 68\,700\,\text{M}^{-1}\,cm^{-1}$) and 532 nm ($\varepsilon = 53\,000\,\text{M}^{-1}\,cm^{-1}$), respectively, whereas that of D102 in THF is located at $\lambda = 494$ nm ($61\,000\,\text{M}^{-1}\,cm^{-1}$).[7a] Adsorption of the indoline dyes on the surface of the mesoscopic TiO_2 films broadens their absorption spectrum, and a shift of the peak maxima to the red results most likely from the formation of J aggregates.[7c]

Figure 2a shows the current–voltage characteristics of the IL-based DSCs obtained with the three indoline sensitizers. The detailed photovoltaic performance parameters under various light densities are listed in Table 1. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (η) obtained with D205 are $13.73\,mA\,cm^{-2}$, 728 mV, 0.719, and 7.18%, respectively. The 7.2% power conversion efficiency is a record for a DSC based on ILs and organic dyes. An even higher efficiency of 7.9% was obtained upon reducing the lamp intensity to $300\,W\,m^{-2}$. At the lower light level photocurrents are smaller, decreasing the mass-transfer-related losses in J_{sc} and FF that are witnessed as a rule with ionic liquids under full solar power.

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[**] We are grateful to Dr. C. Grätzel and Z. Zhang for helpful discussion, P. Comte for TiO_2 film fabrication, and R. T. Koyanagi (CCIC (Japan)) for providing the 400-nm-sized TiO_2 particles. We gratefully acknowledge the Swiss National Science Foundation for financial support.

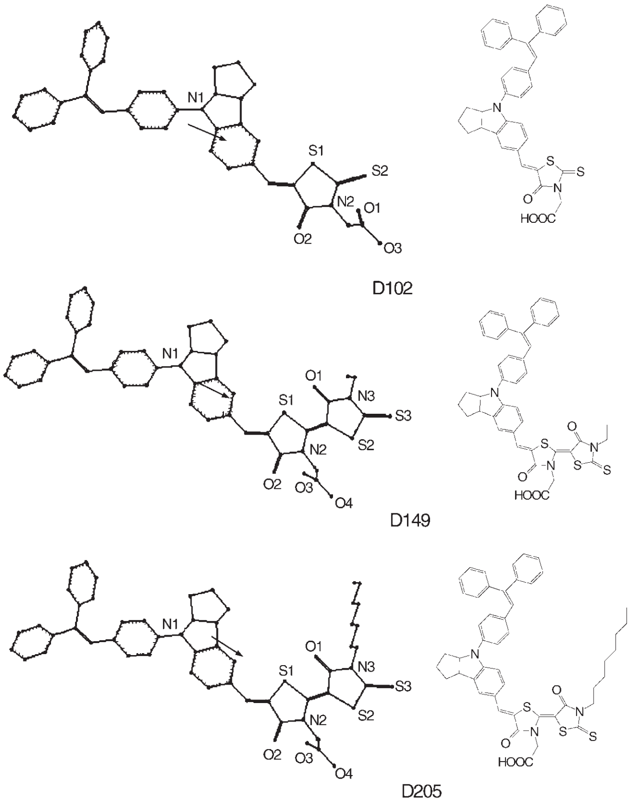

Figure 1. Molecular structures of D102, D149, and D205 sensitizers and their dipole moments (arrow direction points from positive to negative charge).

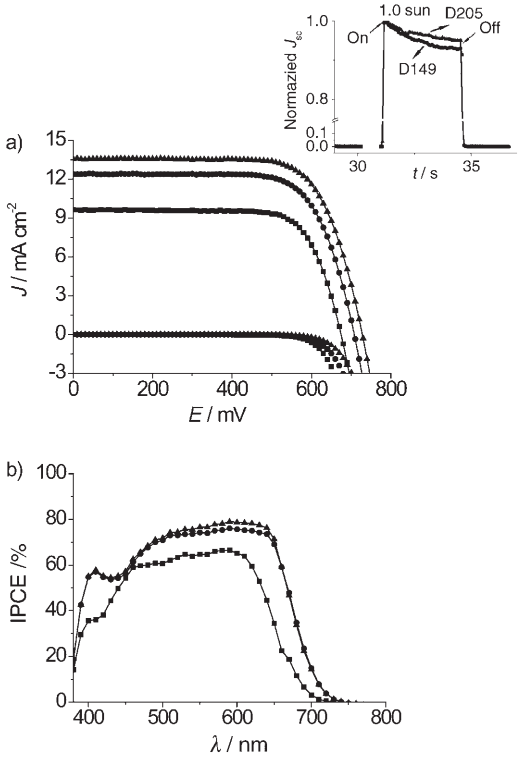

Figure 2. a) Current density–voltage characteristics and b) photocurrent action spectra of the ionic liquid electrolyte based DSCs for devices with D102 (■), D149 (●), and D205 (▲) sensitizers, respectively. IPCE = incident photon to current conversion efficiency. Inset in (a): current dynamics obtained under one sun light illumination for D149 and D205 dyes. Note that the fraction of the photocurrent that decays after opening the light shutter is smaller for the D205 than for D149.

Table 1: Photovoltaic parameters of the IL-based DSCs with D102, D149, or D205 sensitizers under AM 1.5 sunlight at various light intensities.[a]

	Light intensity	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	η [%]
D102	1.0 sun	9.71	674	0.742	4.86
	0.52 sun	5.34	657	0.771	5.11
	0.3 sun	3.15	643	0.783	5.19
D149	1.0 sun	12.52	707	0.720	6.38
	0.52 sun	6.97	692	0.777	7.01
	0.3 sun	4.14	677	0.785	7.21
D205	1.0 sun	13.73	728	0.719	7.18
	0.52 sun	7.5	710	0.766	7.71
	0.3 sun	4.44	696	0.781	7.92

[a] The spectral distribution of the xenon lamp simulates AM 1.5 solar light. The mismatch has been corrected to correspond to AM 1.5 global sunlight (100 mW cm^{-2}). The active area of the cell confined by a black metal mask is 0.158 cm^{-2}.

The superior performance of the D205 dye relative to D149 is particularly noteworthy. As the chromophoric units of these two dyes are identical, the increase in the values of V_{oc} and J_{sc} can be traced to the extension of the alkyl chain on the terminal rhodanine moiety from ethyl to octyl. Importantly, this result shows that substantial gains in the two key photovoltaic performance parameters can be made by subtle changes in the structural design of the sensitizer, thus providing useful clues for the molecular engineering of efficient organic charge-transfer sensitizers.

Further analysis was carried out to unravel the cause for this intriguing behavior. The dark current curves in Figure 2a indicate that D205 has a more negative onset potential for the reduction of I_3^- than the D102 or D149 dyes. One possible explanation for this observation is that the rate constant of reaction of free TiO_2 conduction-band electrons with triiodide ions at a given forward bias potential is decreased by extending the length of the alkyl group on the indoline sensitizer. For example, the amphiphilic nature of D205 may facilitate the formation of a self-assembled dye monolayer that blocks the recapture of the photoinjected electrons by the triiodide ions, resulting in a higher open-circuit voltage and short-circuit current. Alternatively the lower dark current could also be rationalized in terms of a negative shift in the conduction band edge of the TiO_2 caused by the adsorption of the D205 dye.

Electrochemical impedance spectroscopy (EIS) analysis[16,17] was performed to elucidate the photovoltaic findings further. Figure 3 compares data for D102-, D149-, and D205-sensitized cells measured in the dark under a forward bias of −0.70 V. The Nyquist plots (Figure 3a) show the radius of the middle semicircle to increase in the order D102 < D149 < D205, indicating that the electron recombination resistance augments from D102 to D205. The electron lifetime values derived from curve fitting are 6.4, 10.9, and 23.0 ms, respectively. The longer electron lifetime observed with D205-

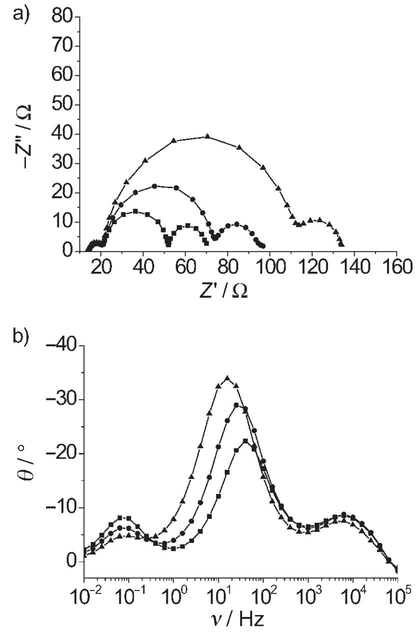

Figure 3. Impedance spectra of DSCs based on D102 (■), D149 (●), and D205 (▲) dye measured at −0.70 V bias in the dark. a) Nyquist plots, b) Bode phase plots.

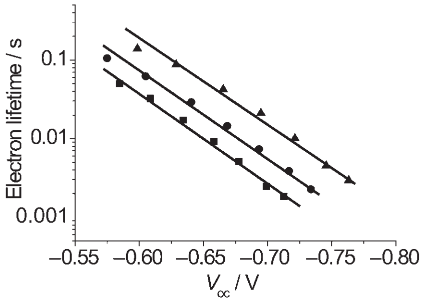

Figure 4. Electron lifetimes of devices based on binary IL electrolyte and D102 (■), D149 (●), or D205 (▲) sensitizers at open-circuit voltage under various light bias.

relative to D149- or D102-sensitized cells indicates more effective suppression of the back reaction of the injected electron with the I_3^- in the electrolyte and is reflected in the improvements seen in the photocurrent and photovoltage, yielding substantially enhanced device efficiency.

The Bode phase plots shown in Figure 3 b likewise support the differences in the electron lifetime for TiO_2 films derivatized with the three dyes. The middle-frequency peak of the DSCs based on D205 shifts to lower frequency relative to D149 and D102, indicating a shorter lifetime for the latter species. The low- and high-frequency peaks observed in the Bode plots correspond to triiodide diffusion in the electrolyte and charge transfer at the counter electrode, respectively. There is no significant change in the position of the high-frequency peaks for the three dyes studied, whereas the low-frequency maximum is at slightly higher frequency for D205 than the two other dyes. Apparently the triiodide diffusion in the porous network is somewhat enhanced in the case of the amphiphilic D205 sensitizer. This result is in keeping with the behavior of the current dynamics shown as an inset in Figure 2 a, which compared the D149 and D205 dyes under full sun illumination. In this case, the fraction of the photocurrent that decayed after opening the light shutter was smaller for D205 than for D149. It is likely that aggregate formation by D149 impairs the transport of the triiodide ions in the pores of the TiO_2 film, thus increasing the diffusion impedance.

Photocurrent and photovoltage transient studies were performed to scrutinize further the strikingly different photovoltaic behavior of the three indoline dyes. Figure 4 shows electron lifetimes of DSCs based on D102, D149, or D205 dyes under corresponding V_{oc} values resulting from various bias light intensities. The measured electron lifetimes of DSCs based on D205 dye are seen to be longer than those utilizing D102 and D149 dyes under various open-circuit potentials. This observation can be ascribed to the effective suppression of electron recombination, which is in agreement with the EIS results described above. The electron lifetime values of DSCs based on D102, D149, and D205 measured at a potential of −0.7 V are 2.6, 5.3, and 14.3 ms, respectively, are smaller than those obtained from the EIS data. These differences can be rationalized in terms of different local I_3^- concentrations present in the pores of the nanocrystalline TiO_2 film and different concentrations of conduction-band electrons. Photovoltage transient decay studies of the DSC performed under illumination refer to a higher I_3^- concentration than that found in the EIS experiments that were measured in the dark.

The electron charge in the TiO_2 films can be calculated from the chemical capacitance by using the relation DOS (density of trap states) $= 6.24 \times 10^{18} C/(d(1-p))$, where d is the thickness of the TiO_2 film, p is the porosity, and C is the capacitance per cm^2. Figure 5 shows the relation of charge in the TiO_2 layer versus photovoltage for the DSCs based on the three different organic dyes, which implies that the band edge shifts increasingly negatively for the dyes in the sequence D102 to D149 to D205. The difference between D205 and D149 is approximately 20 meV, which agrees well with the observed shift in the V_{oc} value. Therefore, the lower rate of electron recapture by triiodide results mainly from a negative shift in the conduction band edge by the adsorbed dye.[18]

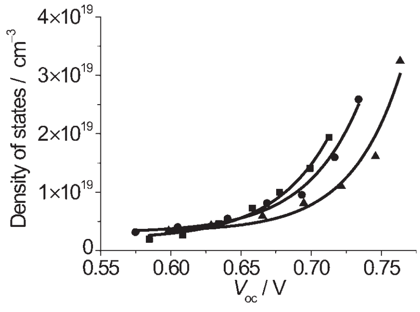

Figure 5. The calculated density of electron trapping states in the mesoscopic TiO_2 film as a function of V_{oc} for DSCs based on the organic dyes D102 (■), D149 (●), and D205 (▲).

The underlying reason for inducing this band movement remains to be fully assessed. One could argue that it is caused by contributions of the dye dipole to the surface potential of the TiO_2 film. The ground-state dipole of the three dyes in vacuum was calculated by an ab initio method (DFT-B3LYP-6-31G*). D102, D149, and D205 have values of 7.26, 7.98, and 7.89 debyes, respectively; the positions of the dipoles are indicated by arrows in Figure 1. The values calculated correlate well with the observed strong absorption bands of their electronic spectra. The calculated dipoles for D102 and D149 would suggest that a band shift is not totally unexpected in the absence of screening of the dipole field by solvent molecules and ions present in the interface. The magnitude is consistent with the small observed V_{oc} shift for constant charge density. However, a further shift of 25 mV for the D205 dye cannot be explained in terms of the dipole alone. An advantageous change in surface orientation and packing dictated by the octyl chain has to be invoked.

It is clear that the three dyes moderate the electron recombination rate constant, as seen in Figure 4, but this parameter reflects the kinetics of trapped and not free conduction-band electrons and hence is sensitive to changes in the energetic position of the traps. The latter in turn depends on the position of the conduction band edge. Thus, the interplay of movement and recombination of the band edge on cell performance needs to be considered. Since the measured charge density versus photovoltage shows variation as a function of the adsorbed dye it appears that a shift in the TiO_2 conduction band is mainly implicated.

Experimental results reported on three organic dyes (indoline based; D102, D149, D205) underline the importance of augmenting the photovoltaic performance by appropriate molecular design. Thus, endowing the sensitizer with an octyl chain was highly effective in suppressing electron recombination, as shown by the enhanced electron lifetimes. Judicious molecular design in the development of organic sensitizers led to a record power conversion efficiency of 7.2% under AM 1.5 full sunlight intensity using an ionic-liquid-electrolyte-based DSC.

Experimental Section

The mesoscopic anatase TiO_2 films were screen-printed on F-doped tin oxide conducting glass (FTO) as previously described.[19] A 5-μm-thick scattering layer of 400-nm particles obtained from CCIC Inc. (Japan) was superimposed on a 7-μm transparent layer of 20-nm particles. The films were stained with the sensitizer by dipping for 16 h in a 0.3 mM solution of the respective dye in a mixture (volume ratio 1:1) of acetonitrile and *tert*-butyl alcohol. *N*-butyl benzimidazole (NBB) was synthesized according to a published procedure.[6] The synthesis of 1-ethyl-3-methyl-imidazolium tetracyanoborate ($EMIB(CN)_4$) was reported earlier (the studies described herein employed a sample supplied by Merck).[20] The binary ionic liquid electrolyte consisted of 0.2 M iodine, 0.5 M NBB, and 0.1 M GuNCS in a mixture of PMII and $EMIB(CN)_4$ (volume ratio 65:35). The assembly and photovoltaic characterization of the devices were described in detail elsewhere.[4] Impedance measurements were performed with a computer-controlled potentiostat (EG&G, Model 273) equipped with a frequency response analyzer (EG&G, Model 1025). Transient photovoltage measurements employed a 200-ms exciting pulse generated by a ring of red light emitting diodes (LEDs, Lumiled) controlled by a fast solid-state switch. The pulse was incident on the TiO_2 side of the device and its intensity was controlled to keep the modulation of the voltage below 5 mV so that the relaxation kinetics were of first order. White bias light impinging the cell from the same direction was also supplied by LEDs. Transients were measured at different white light intensities ranging from 150% to 0.1% of AM 1.5 solar light ($1000\ W\,m^{-2}$) and adjusted by tuning of the voltage applied to the bias diodes.

Received: November 13, 2007

Keywords: dyes/pigments · impedance spectroscopy · ionic liquids · sensitizers · solar cells

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