Efficient Electron Transfer and Sensitizer Regeneration in Stable $\pi$-Extended Tetrathiafulvalene-Sensitized Solar Cells

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Abstract: The development of metal-free organic sensitizers is a key issue in dye-sensitized solar cell research. We report successful photovoltaic conversion with a new class of stable tetrathiafulvalene derivatives, showing surprising electrochemical and kinetic properties. With time-resolved spectroscopy we could observe highly efficient regeneration of the photo-oxidized tetrathiafulvalene sensitizers, which were attached to a mesoporous TiO$_2$ film, by a redox mediator in the pores (iodide/tri-iodide), even though the measured driving force for regeneration was only $\sim$150 mV. This important proof-of-concept shows that sensitizers with a small driving force, i.e., the oxidation potential of the sensitizer is separated from the redox potential of the mediator by as little as 150 mV, can operate functionally in dye-sensitized solar cells and eventually aid to reduce photovoltage losses due to poor energetic alignment of the materials.

Introduction

Dye-sensitized solar cells (DSCs) can convert solar radiation into electricity efficiently and cost-effectively by means of a light-harvesting sensitizer anchored to a high surface area mesoporous semiconductor film. Record efficiencies of over 11% have been measured with ruthenium-complex sensitizers and promising device efficiencies of up to 9.8% have been demonstrated with a donor-$\pi$-acceptor system employing a triphenylamine donor, a binary $\pi$-conjugated spacer, and a cyanoacrylic acid acceptor.

Here we investigate the photovoltaic potential of sensitizers with a tetrathiafulvalene derivative donor and a cyanoacrylic acid acceptor in DSCs. Tetrathiafulvalenes with extended $\pi$-conjugation (exTTF) are a well-known class of electron donor systems. Several studies have investigated charge transfer events in exTTFs attached to fullerenes and to single-walled carbon nanotubes. The out-of-plane butterfly shape of the exTTF provides steric hindrance, preventing self-aggregation of the sensitizer, a significant parameter in the performance of DSCs. The exTTF sensitizer is attached to a mesoporous TiO$_2$ film, by a redox mediator in the pores (iodide/tri-iodide), even though the measured driving force for regeneration was only $\sim$150 mV. This important proof-of-concept shows that sensitizers with a small driving force, i.e., the oxidation potential of the sensitizer is separated from the redox potential of the mediator by as little as 150 mV, can operate functionally in dye-sensitized solar cells and eventually aid to reduce photovoltage losses due to poor energetic alignment of the materials.
film, to which it transfers an electron after photoexcitation. A surrounding redox mediator (iodide/tri-iodide couple) rapidly regenerates the oxidized sensitizer to prevent reduction by the injected electron. We provide a careful spectroscopic characterization and kinetic analysis of the formation of the oxidized sensitizer and its highly efficient regeneration by iodide, documenting for the first time efficient sensitizer reduction in DSCs with as little as a 150 mV driving force between the redox potential of the iodide/tri-iodide mediator and the oxidation potential of the sensitizer.

A series of three new exTTF sensitizers (PAB-1, PAB-2, and PAB-3, shown in Figure 1) was designed and synthesized in moderate yields by Knoevenagel condensation from the respective exTTF-based aldehydes. The sensitizers, which have in common the donor (exTTF) and acceptor/anchoring (cyanooacrylic acid) group, are differentiated by the extent of \( \pi \)-conjugation in the spacer. In PAB-3, an electron-rich 3,4-ethylenedioxythiophene (EDOT) unit is used to considerably enhance its molar extinction coefficient. EDOT spacers have been successful in red-shifting the spectral response and enhancing the molar extinction coefficient of triphenylamine donor sensitizers.\(^7,15\) In addition, we synthesized an analogue of PAB-3 with a TTF donor, coded PAB-4, to elucidate the conformational effect of a more planar molecule on self-aggregation and photovoltaic performance. As shown in the Supporting Information, absorbance spectra suggest aggregation on the TiO\(_2\) film, which might be responsible for the poor photovoltaic performance.

**Experimental Section**

**Synthesis.** Materials, synthesis of the sensitizers, and full characterization are provided in the Supporting Information (SI).

**Electrochemical Measurements.** Electrochemical data were obtained by differential pulse voltammetry (DPV) using a PC-controlled AutoLab system (PGSTAT-10, Eco Chemie). The electrochemical cell was assembled and measured in an Ar-filled glovebox. The glassy carbon disk working electrode (Metrohm), electrochemical cell was assembled and measured in an Ar-filled glovebox. The Pt-plate auxiliary electrode, and Pt-wire quasi reference electrode were immersed for 5 h in a solution of 0.3 mM dye and 10 mM cheno in a mixture of dimethyl sulfoxide (DMSO) and ethanol (1/9 v/v). Cells were sealed with a platinized FTO counter electrode using a hot-melt (Surlyn, DuPont). Cells were then filled with an electrolyte through a hole in the counter electrode. The hole was then sealed with a Surlyn disk and a thin glass to avoid leakage of the electrolyte. We compared the photovoltaic performance using a volatile solvent-based electrolyte (coded as Z960) and an ionic liquid electrolyte (coded as Z952). The composition of electrolytes was as follows: Z960: 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tetr-butylpyridine, 0.05 M LiI in a mixture of acetonitrile and valeronitrile (85/15, v/v). Z952: 1,3-dimethylimidazoliumiodide/1-ethyl-3-methylimidazoliumiodide/1-ethyl-3-methylimidazolium tetracyanoborate/ iodine/N-butylbenzoimidazole/guanidinium thiocyanate (molar ratio 12/12/16/3.33/0.67). The photoanode was covered with a UV_cutoff/antireflecting polymer.

**Photovoltaic Characterization and Stability Tests.** A 450 W xenon light source (Oriel, USA) was used to give an irradiance of 100 mW cm\(^{-2}\) (the equivalent of one sun at air mass global, AM 1.5G, at the surface of solar cells). The spectral output of the lamp was matched in the region 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and true solar spectra to less than 2%. The current–voltage characteristics of the cell were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). The effective area of the devices was defined with a metal mask to be 0.159 cm\(^2\).

A similar data acquisition system was used to control the incident photon to collected electron conversion efficiency (IPCE) measurement. Under computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. A computer controlled monochromator was incremented through the spectral range (300–900 nm) to generate a photocurrent action spectrum with a sampling interval of 10 nm and a current sampling time of 5 s.


For stability tests, devices were irradiated at open circuit under a Suntest CPS plus lamp (ATLAS GmbBH, 100 mW cm\(^{-2}\)) in ambient air at 60 °C.

**Transient Photovoltage Decay Measurements.** Transient decays were measured with different white light steady-state biases and a superimposed red light perturbation pulse (0.05 s square pulse width, 100 ns rise and fall time), incident on the photoanode side of the test device. The white and red light were supplied by light-emitting diodes. The voltage dynamics were recorded at open circuit on a PC-interfaced Keithley 2400 source meter with a 500 μs response time. The perturbation light source was set to a suitable low level for the voltage decay kinetics to be monoeponential. By varying the white light bias intensity, the recombination rate constant could be estimated at open-circuit potentials of the device (corresponding to different free charge densities in the TiO\(_2\) film).

**Nanosecond Laser Transient Absorbance Measurements.** Transparent nanocrystalline anatase TiO\(_2\) films (4.8 nm thick, 16 nm particle diameter, porosity = 0.625) were coated with PAB-1, PAB-2, or PAB-3 dye for ~12 h. The samples were excited by pulses produced by a broad-band optical parametric oscillator (OPO GWU-355) pumped with a Continuum Powerlite 7030 frequency-tripled (i.e., 355 nm) Q-switched Nd:YAG running at 30 Hz. The output excitation wavelength was tuned at \(\lambda = 505\) nm with a pulse width of 7 ns (fwhm). The pulse energy was attenuated with neutral density gray filters down to 30 μJ cm\(^{-2}\), a fluence under which our samples exhibit, on average, less than one injected electron per nanoparticle. The probe light was produced by a Xenon arc lamp. This light was filtered through a monochromator and diverse filters, focused onto the sample, and then collected in a second monochromator. It was then detected by a fast photomultiplier tube biased with 750 V. Averaging over 1000 to 2000 laser shots was necessary to obtain satisfactory signal-to-noise ratios. A combination of several transients, recorded at different wavelengths, permits us to reconstruct a transient spectrum.

**Results and Discussion**

**Electronic Absorption and Redox Behavior.** The absorbance spectra of the sensitizers in dimethylsulfoxide and anchored to a transparent mesoporous TiO\(_2\) film are shown in Figure 2. The absorption peak of PAB-1 at 399 nm (extinction coefficient \(\varepsilon = 14.1 \times 10^3\) M\(^{-1}\) cm\(^{-1}\)), PAB-2 at 411 nm (\(\varepsilon = 25.1 \times 10^3\) M\(^{-1}\) cm\(^{-1}\)), and PAB-3 at 419 nm (\(\varepsilon = 36.0 \times 10^3\) M\(^{-1}\) cm\(^{-1}\)) are attributed to \(\pi-\pi^*\) charge transfer transitions in the exTTF chromophores. The gradual increase in \(\varepsilon\) and the slightly red-shifted absorbance peaks are due to the extended \(\pi\)-conjugation in the spacer. In sensitized TiO\(_2\) films we observe a small red shift of the peak for PAB-1 (414 nm) and PAB-2 (416 nm) and a blue shift for PAB-3 (404 nm), which is attributed to the coupling of the carboxylate moiety with the semiconductor. Notably, blue shifts have been previously observed with organic sensitizers containing an EDOT spacer.\(^{15}\) The concentration of dye molecules adsorbed on the TiO\(_2\) film was estimated by desorbing sensitized films with tetrabutylammonium hydroxide in a \(N,N'\)-dimethylformamide solution. A similar dye loading was obtained for PAB-1 and PAB-2 (\(c = 0.13\) M), and slightly better packing behavior on the TiO\(_2\) surface was seen for PAB-3 (\(c = 0.16\) M).

The electrochemical oxidation of the exTTF chromophore was previously reported as an overall two-electron process\(^{17-19}\) occurring with potential inversion; i.e. the second electron is removed more easily than the first. The extent of potential inversion is estimated to be \(\sim 0.16\) V from simulations of cyclic voltammograms.\(^{20}\) Formation of the short-lived radical cation and its disproportionation into the stable dication has been studied with radiolytic oxidation\(^{21}\) and flash photolysis techniques.\(^{22}\)

The electrochemical properties of the sensitizers were assessed with differential pulse and cyclic voltammograms in a dimethylformamide (DMF) solution using tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) as a supporting electrolyte and referenced to the ferrocinium/ferrocene (Fc\(^+/\)Fc) couple.

Interestingly, the two-electron oxidation potential \((E_{ox})\) of the compounds (Figure 3 and Table 1), indicating the highest occupied molecular orbital (HOMO), is up to 300 mV more negative than the \(E_{ox}\) of a standard Ru-complex sensitizer (+0.16 V vs Fc\(^+/\)Fc).\(^{16}\) The one-electron oxidation potential (PAB-1 → PAB-1\(^+\)) is estimated to be 80 mV more positive due to potential inversion.\(^{20}\) Consequently, the driving force for regeneration of the oxidized species by the I\(^-\)/I\(_2\) redox mediator (−0.21 V vs Fc\(^+/\)Fc in ionic liquid)\(^{23}\) is as low as 150 mV.


note that the Fe⁺/Fe couple is a suitable reference for these compounds, since their $E_{ox}$ peak is well distinguished from the reference peak (Figure S1). The reduction potential ($E_{red}$) of the dyes, indicating their lowest unoccupied molecular orbital (LUMO), is considerably more negative than the TiO₂ conduction band, providing ample driving force for electron transfer.

Density functional theory (DFT) calculations were performed with the Spartan software package using the B3LYP hybrid functional and the 6-31+G basis set to investigate the electronic properties of the sensitizers. The orbital energy levels in vacuum, minimum energy conformations, and electron density plots are shown in Figure S2. The well-known structure of the neutral state is saddle-shaped.¹⁹,²⁴ The HOMOs of PAB-1 and PAB-2 are at a similar energy level, whereas the HOMO of PAB-3 is raised due to the high electron density in the EDOT spacer. The LUMOs of PAB-2 and PAB-3 are lower than the LUMO of PAB-1 due to the extended π-conjugation in the spacer. In all three cases, the HOMO is delocalized over the anthracene and dithiole units, and the LUMO is delocalized over the cyanoacrylic acid group, facilitating electron transfer from the excited state to the TiO₂ conduction band $\text{via}$ the carboxylate anchoring group.

**ATR-FITR Spectra.** The ATR-FTIR spectra of the sensitizers in powder form and anchored on a mesoporous TiO₂ film are shown in Figure S3. The powder spectra show a distinct band at 1700 cm$^{-1}$ for the $\text{C=O}$ stretch in the carboxyl group. This band is not observed in the spectra of the sensitized films. Instead, the spectra clearly show bands at 1630 cm$^{-1}$ and 1385 cm$^{-1}$ for the asymmetric and symmetric stretching modes of the carboxylate groups, indicating that the carboxylic acid is deprotonated and involved in the adsorption of the dye on the TiO₂ surface.

**Photovoltaic Performance.** The photovoltaic performance of the sensitizers, i.e., the incident photon-to-current conversion efficiency (IPCE) and the photocurrent–voltage ($J-V$) curve, was assessed in test devices using standard mesoporous 5 μm thick TiO₂ films and a volatile acetonitrile-based electrolyte. The device fabrication and electrolyte composition are described in the Experimental Section. The IPCE in Figure 4a shows peak values of 48% at 510 nm for PAB-1, 54% at 520 nm for PAB-2, and 72% at 460 nm for PAB-3 in accordance with the shape and magnitude of the respective extinction coefficients. From an estimation of the fraction of absorbed photons in the TiO₂ film (using the Lambert–Beer law), we find that between 87% (PAB-1) and close to 100% (PAB-3) of the incident light is absorbed in the TiO₂ film at the respective absorption peak wavelength. Accounting for ~10% total reflection and absorbance losses in the fluorine-doped tin oxide front electrode, this implies an up to 30% higher fraction of absorbed photons than measured IPCE. We assume an injection efficiency close to unity implying an up to 30% higher fraction of absorbed photons than measured IPCE. Instead, the spectra clearly show bands at 1630 cm$^{-1}$ and 1385 cm$^{-1}$ for the asymmetric and symmetric stretching modes of the carboxylate groups, indicating that the carboxylic acid is deprotonated and involved in the adsorption of the dye on the TiO₂ surface.

### Table 2. Photovoltaic Parameters of Devices with a 5 μm Thick TiO₂ Film and Volatile Electrolyte under Simulated AM 1.5G Illumination (100 mW cm$^{-2}$)

<table>
<thead>
<tr>
<th>Dye</th>
<th>η (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAB-1</td>
<td>2.9</td>
<td>555</td>
<td>-7.2</td>
<td>0.72</td>
</tr>
<tr>
<td>PAB-2</td>
<td>3.2</td>
<td>578</td>
<td>-7.7</td>
<td>0.73</td>
</tr>
<tr>
<td>PAB-3</td>
<td>3.8</td>
<td>579</td>
<td>-8.6</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Figure 4. IPCE (a) and photocurrent–voltage (b) curves of test devices with 5 μm thick TiO₂ films, sensitized with PAB-1, PAB-2, or PAB-3, and volatile electrolyte under full 100 mW cm$^{-2}$ simulated AM 1.5G sunlight (continuous lines) and in the dark (dotted lines). In Figure 4b, and corresponding photovoltaic parameters, i.e., the conversion efficiency (η), short-circuit photocurrent density ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), and the fill factor (FF), are given in Table 2. The increase in efficiency from 2.9% (PAB-1) to 3.8% (PAB-3) is largely due to an increase in photocurrent, in agreement with the measured IPCEs, and an associated small increase in photovoltage. Overall, the measured photovoltage is relatively low. With state-of-the-art DSCs one can expect a $V_{oc}$ of over 750 mV at comparable current densities. This is a further indication for substantial charge recombination losses.

**Photovoltage Decay Transients.** We measured the photovoltage decay transients of devices with the volatile electrolyte at various white light bias intensities to study the charge recombination rates ($k_c$) between electrons in the TiO₂ conduction band and tri-iodide ions in the electrolyte. In Figure 5, $k_c$ is plotted versus the open-circuit potential ($V_{oc}$) induced by the white light bias. We note that the electron lifetime $\tau_e = k_c^{-1}$ is in the ms range. Since the $V_{oc}$ in the device is given by the difference between the redox level of the electrolyte and the quasi-Fermi level in the TiO₂, which is determined by the concentration of free charge carriers, this plot allows us to compare $k_c$ at equal charge density concentrations in the TiO₂ film. $k_c$ is known to increase exponentially with increasing bias light due to the filling of intraband trap states in the TiO₂, which allows for a faster detrapping of electrons to the conduction band and subsequent detrapping.


recombination with tri-iodide. We measured a gradually decreased $k_r$ with an increased spacer distance in the sensitizers, i.e. the highest $k_r$ with PAB-1 and an $\sim 2.6$ times reduced rate with PAB-3, which we attribute to the improved dye packing on the surface. However, the $k_r$ of the device with PAB-3 is still two orders of magnitude higher than the rate of a state-of-the-art device with a ruthenium-complex dye. Increased recombination and, consequently, low $V_{oc}$ have been observed for many classes of organic sensitizers and might be catalyzed by the formation of an iodine/dye complex.

Nanosecond Laser Transient Absorbance Measurements. We used time-resolved spectroscopy on sensitized TiO$_2$ films to probe the formation of the radical cation (1), its interception by iodide (2), and a possible disproportionation of the radical cation into the dication (3). The oxidation of the nonfunctionalized exTTF chromophore is well-known; the short-lived radical cation into the dication (3). The oxidation of the nonfunctionalized exTTF chromophore is well-known; the short-lived radical cation at 650 nm. The time-dependent signature (PAB-1) shows a fingerprint at $\sim 650$ nm and rapidly disproportionate into the stable dication.$^{21,22}$

The transient absorption spectrum of a PAB-1 sensitized film in Figure 6a (no redox mediator) clearly shows the signature of the radical cation at 650 nm. The time-dependent signature at 650 nm of films sensitized with PAB-1, PAB-2, or PAB-3 is depicted in Figure 6b. In the absence of a redox mediator (only acetonitrile, ACN), the decay can be fitted with a monoeponential function with a time constant of $\tau = 2.3$ ms ($k_0 = 435$ s$^{-1}$) for PAB-1, $\tau = 256$ $\mu$s for PAB-2, and $\tau = 494$ $\mu$s for PAB-3, reflecting the lifetime of the radical dye cation when reduced only by electrons from the TiO$_2$ conduction band (4). In the presence of a redox mediator (ACN-based redox electrolyte), the decay is accelerated by two to three orders of magnitude ($\tau = 7.4$ $\mu$s, $k_0 = 1.35 \times 10^8$ s$^{-1}$ for PAB-1; $\tau = 18$ $\mu$s for PAB-2; $\tau = 25$ $\mu$s for PAB-3) due to rapid interception of the cation by iodide (2). These time scales are similar to

\begin{align*}
S^+ \rightarrow S^{++} + e_{cb} & \\
S^{++} + 2\Gamma^- \rightarrow S + \Gamma^- \text{ and } 2\Gamma^- \rightarrow \Gamma_3 + \Gamma^- & \\
S^{++} + S^{++} \rightarrow S^{++} + S & \\
S^{++} + e_{cb}^- \rightarrow S & (1) \\
(2) \\
(3) \\
(4)
\end{align*}

values reported for Ru-based sensitizers.$^{28}$ The dye regeneration yield by iodide, given by the $k_f/(k_0 + k_r)$ ratio, exceeds 99% for PAB-1 and 93% for PAB-3. This finding is remarkable, as it shows that a very small driving force of $\sim 150$ mV between the redox potential of the electrolyte and the oxidation potential of the sensitizer is sufficient for efficient regeneration of the cation. The transient signature of PAB-1 at 550 nm in ACN only (Figure 6c) shows an initial bleaching of the ground state after charge injection. Recovery of the dye absorption takes place with a half reaction time of $\tau = 55$ $\mu$s. The positive signal observed $>50$ $\mu$s after the laser pulse excitation is attributed to the dication absorption. The kinetic process is thus likely to be due to the dye cation disproportionation (3). In the presence of the electrolyte, this positive absorbance disappears completely, and only a fast recovery of the ground state is observed with $\tau = 4.6$ $\mu$s (the rapid component of a double-exponential fit), corresponding to the kinetics of the reduction of dye cations by iodide observed in the red spectral region. Consequently,
little dication species should be formed in a working cell under full sunlight illumination.

**Device Stability.** We finally tested the long-term stability of the most promising PAB-3 sensitizer in devices with a solvent-free ionic liquid electrolyte (composition given in the Experimental Section) during 1000 h of full sunlight illumination (AM 1.5G, 100 mW cm$^{-2}$) at 60 °C. The evolution of the photovoltaic parameters is shown in Figure 7. Parameters are normalized to the stabilized values after 120 h of light soaking ($\eta = 2.7\%$, $J_{sc} = -6.8$ mA cm$^{-2}$, $V_{oc} = 534$ mV, FF = 0.74).

**Conclusions**

We have successfully demonstrated photovoltaic energy conversion in stable $\pi$-extended tetrathiafulvalene-sensitized solar cells. Compared to standard ruthenium-complex sensitizers, these new dyes show an up to 300 mV more negative oxidation potential, which could impair efficient reduction by the redox mediator. With time-resolved spectroscopy, however, we could prove for the first time that efficient regeneration of sensitizers with as little as a 150 mV driving force between the oxidation potential of the sensitizer and the redox potential of the mediator is possible. Since large driving forces imply a loss in photovoltage, this finding provides a valuable proof-of-principle for the use and design of efficient sensitizers with a low regeneration driving force for high efficiency dye-sensitized solar cells.

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**Supporting Information Available:** Synthesis methods and characterization, supplementary voltammetric results, calculated molecular orbital levels, and ATR-FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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