This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Deposition of loosely bound organic D-A-π-A’ dyes on sensitized TiO₂ film: a possible strategy to suppress charge recombination and enhance power conversion efficiency in dye-sensitized solar cells

Xiongwu Kang,† Junxiang Zhang,† Anthony J. Rojas, Daniel O’Neil, Paul Szymanski, Seth R. Marder* and Mostafa El-Sayed*

†Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, United States; melsayed@gatech.edu

‡School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, GA 30332-0400, United States; seth.marder@chemistry.gatech.edu

ABSTRACT
A D-A-π-A’ dye (coded as AR-II-13) – composed of a triarylamine donor, a difluorobenzothiadiazole internal acceptor and a cyanoacrylic acid anchoring acceptor – has been successfully synthesized via sequential C-H direct arylation, and used as sensitizer in dye-sensitized solar cells (DSSCs). The butoxy group at the donor side and the hexyl group on di-substituted cyclopenta[1,2-b:5,4-b’] dithiophene (CPDT) bridge are incorporated to decrease dye aggregation and offer physical insulation between electrolyte oxidant and TiO$_2$ films. It is demonstrated that the open circuit voltage ($V_{OC}$), short circuit current ($J_{SC}$) and power conversion efficiency ($PCE$) are remarkably enhanced relative to a conventionally fabricated cell by deposition of additional dye on the sensitized TiO$_2$ films. The impact of dye bath solvent on dye aggregation was observed to be minimal and the enhancement of solar cell performance was exclusively ascribed to the loosely bound dye moieties providing physical insulation on TiO$_2$ films from I$_3^-$ and retarding charge recombination between electrons in the TiO$_2$ film and the electrolyte, as confirmed by electrochemical impedance measurements. Furthermore, the dipole interaction between the TiO$_2$ surface and loosely bound dye may play a synergetic role in enhancing the photovoltaic performance of the resulting devices, cooperatively.

**Introduction**

Dye sensitized solar cells (DSSCs), a type of photovoltaic devices made of transparent conductive glasses, solution-processed titanium oxide nanoparticles and organic dye molecules, have been extensively studied and developed as a promising alternative to silicon photovoltaics due to their low manufacturing cost and excellent photovoltaic performance. Since the breakthrough of power conversion efficiency ($PCE$) of DSSCs based on mesoporous films made of colloidal TiO$_2$ nanoparticles was first reported in 1991,$^1$ a large number of pure organic and organometallic dyes have been synthesized and characterized, and the solar to electric $PCE$ has been advanced to 12%.$^{2,3}$
However, the photovoltaic performance of the DSSCs are still limited by a factors such as low photocurrent due to limited light harvesting of low energy photons, low open circuit voltages. For DSSCs using liquid electrolytes based on the I\(^{-}/\text{I}_3^{-}\) redox couple, one of the critical factors that cause low open circuit voltage is charge recombination of the injected electrons in the TiO\(_2\) film with I\(_3^{-}\) electrolyte, which reduces the electron lifetime in TiO\(_2\) films, lowering the Fermi level of TiO\(_2\) films and thus reducing the \(V_{OC}\). Extensive efforts have been devoted to overcoming this problem. For instance, ultrathin layers of insulating metal oxides, such as Nb\(_2\)O\(_5\), \(\text{Al}_2\text{O}_3\), SiO\(_2\), and ZrO\(_2\), have been deposited on top of TiO\(_2\) nanoparticles to prevent the charge recombination between TiO\(_2\) films and electrolyte. However, this technique has a drawback: the thin layer of insulating metal oxides also slows down charge injection from excited state of dye to TiO\(_2\) conduction band and thus lowers the photocurrent.\(^6\) An alternative strategy is to graft the TiO\(_2\) films with dye and co-adsorbents such as chenodeoxycholic acid (CDCA)\(^7\) physically insulating TiO\(_2\) film from electrolyte oxidant, thus suppressing charge recombination. Although some dyes moieties may accelerate the charge recombination process,\(^8\) it has been demonstrated that some sensitizers themselves could efficiently prevent charge recombination. For instance, Koumura\(^11\) have improved the electron lifetime in TiO\(_2\) films by 2 orders-of-magnitude and \(V_{OC}\) by 80 mV through incorporation of several mono-hexyl substituted thiophene groups on \(\pi\)-bridges, which are suggested to keep the electrolyte away from the TiO\(_2\) surface and thus retard the charge recombination rate. Di-substituted cyclopenta[1,2-\(b\):5,4-\(b\')]dithiophene (CPDT) group was first exploited by Wang\(^12\) to improve the \(V_{OC}\) and \(PCE\) of the corresponding dye by 50 mV and 26.7%, with regards to 2,2'-dithiophene as bridge. However, such approaches might not be always effective. For instance, when a CPDT-containing squaraine dye was integrated into cells with I\(^{-}/\text{I}_3^{-}\) electrolyte, the photocurrent was enhanced due to disruption of dye aggregation, but the \(V_{OC}\) also dropped by 10 mV.\(^13\)
Herein, we report a potential approach to suppress charge recombination and enhance the photocurrent and PCE by use of different solvents to deposit the dye on the TiO$_2$ films, in some case loosely bound dyes (defined here as those easily removed by a good solvent, see below).

**Results and Discussion**

In the dye reported here, 4-butoxy-$N$-(4-butoxyphenyl)-$N$-phenylaniline was chosen as a donor, as butoxy group would further increase the electron donating properties of triarylamine group and create barriers between electrons in the titania and holes in the redox couple as well. Recently, it has been found that incorporation of an additional electron-withdrawing unit into the π-system as internal acceptors, termed the D–A–π–A’ configuration, displays extra advantages such as tuning of the molecular energy levels, red-shift of the charge-transfer absorption band, and distinct improvement of photovoltaic performance and stability.$^{14}$ In this sense, we utilized 5,6-difluorobenzo[c][1,2,5]thiadiazole, DFBT, as an internal acceptor to connect the triarylamine with di-$n$-hexyl-substituted cyclopentadithiophene (CPDT) bridge. CPDT with the gem-di-$n$-hexyl substituents extended above and below the π-conjugated dye plane is introduced to prevent dye aggregation.$^{15}$ The synthesis of AR-II-13 is shown in the following scheme. We employed recently-developed sequential direct arylations of DFBT,$^{16}$ to synthesize 3, (1 reported earlier was itself synthesized by reaction of 5,6-difluorobenzo[c][1,2,5]thiadiazole with 4-bromo-$N,N$-bis(4-butoxyphenyl)aniline) in an efficient manner. A final Knoevenagel condensation with cyanoacetic acid in the presence of piperidine yielded the target dye as a black solid.
AR-II-13 exhibits a moderate PCE of 4.9% with conventional device fabrication. However, the $V_{OC}$ and PCE are significantly enhanced by 50 mV and 34.7%, respectively, by depositing a layer of loosely bound dye upon the sensitized TiO$_2$ film. Upon extensive investigation, dye aggregation caused by solvent was ruled out and the enhancement of the $J_{SC}$, $V_{OC}$ and PCE by deposition of loosely bound dye moieties on TiO$_2$ film was exclusively ascribed to the suppression of charge recombination between the TiO$_2$ film and the electrolyte by the physical insulation offered by the loosely bound dye.

Scheme 2. The chart flow of diverse treatment conditions for the sensitized TiO$_2$ films.
Two kinds of devices, which are denoted as D1 and D2, were fabricated by the following procedures. The TiO$_2$ films for these devices were sensitized by dipping for 12 hours in the dye bath with 0.3 mM AR-II-13 and 20 mM CDCA. When being retracted from the dye bath, the sensitized TiO$_2$ films were rinsed with ethanol/chloroform (1:1) and then ethanol for D1 devices, whereas rinsed with ethanol only for D2 devices. The current-voltage profiles for D1 and D2 devices were scanned under one sun illumination and depicted in Figure 1, from which the photovoltaic parameters were derived and listed in Table 1. The \( PCE \) for D1 is 4.9\%, with a \( V_{OC} \) of 0.681 V, and \( J_{SC} \) of 10.0

<table>
<thead>
<tr>
<th></th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm$^2$)</th>
<th>FF(%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1, 0.3 mM$^{(a)}$</td>
<td>0.681 (+0.003)</td>
<td>10.0 (+0.2)</td>
<td>71.1 (+0.2)</td>
<td>4.9 (+0.2)</td>
</tr>
<tr>
<td>D2, 0.3 mM$^{(b)}$</td>
<td>0.730 (+0.003)</td>
<td>12.7 (+0.1)</td>
<td>71.2 (+0.8)</td>
<td>6.6 (+0.1)</td>
</tr>
<tr>
<td>D3, 0.15 mM$^{(a)}$</td>
<td>0.680 (+0.005)</td>
<td>10.5 (+0.1)</td>
<td>71.1 (+0.6)</td>
<td>5.1 (+0.1)</td>
</tr>
<tr>
<td>D4, 0.15 mM$^{(b)}$</td>
<td>0.715 (+0.002)</td>
<td>12.2 (+0.1)</td>
<td>71.0 (+0.1)</td>
<td>6.2 (+0.1)</td>
</tr>
<tr>
<td>D5, 0.3 mM$^{(c)}$</td>
<td>0.723 (+0.003)</td>
<td>12.8 (+0.2)</td>
<td>70.5 (+0.5)</td>
<td>6.6 (+0.1)</td>
</tr>
<tr>
<td>D6, 0.3 mM$^{(d)}$</td>
<td>0.671 (+0.002)</td>
<td>9.7 (+0.3)</td>
<td>72.2 (+1.4)</td>
<td>4.7 (+0.1)</td>
</tr>
</tbody>
</table>
mA/cm$^2$. In remarkable contrast, D2 exhibits a $PCE$ of 6.6%, $V_{OC}$ of 0.73 V, and $J_{SC}$ of 12.7 mA/cm$^2$. With regard to that of D1, the D2 devices demonstrate enhanced $J_{SC}$ by 27%, $V_{OC}$ by 50 mV and $PCE$ by 34.7%.

In addition, the onset potential of dark current for D1 and D2 are 0.45 V and 0.55 V respectively, 0.1 V larger for D2 than D1. Since the dark current are all from the charge recombination of electrons in TiO$_2$ film with electrolyte oxidant, the lower onset potential of dark current in D1 than D2 indicates faster charge recombination rate in the former than the latter.

The only difference of D1 and D2 devices is the solvent used to rinse the sensitized TiO$_2$ films when being retracted from the dye bath. For the former devices, the solvent of ethanol was used while for the latter, a mixture of chloroform/ethanol (1:1) was applied. One question is raised immediately: why is the rinsing solvent so critical for the dye cell performance? At the first glance, we ascribed such differentiation of photovoltaic performance to the varied dye aggregation caused by exposure to different solvent, which has been widely reported.\textsuperscript{17-19} However, in-depth examination, which is depicted in Scheme 2 for clear view and direct comparison, indicates that the varied solubility of dye in different solvents probably results in deposition of loosely bound dye moieties on TiO$_2$ films, which suppresses charge recombination and enhances solar cell performance.

AR-II-13 dye exhibits much higher solubility in chloroform than in ethanol. When retracting and rinsing sensitized TiO$_2$ films in D2 from dye bath solution with ethanol directly deposits loosely bound dye moieties on TiO$_2$ films. How will the deposition of extra dye moieties affect the performance of the dye cells? Intuitively, we may think that light harvesting is not saturated and the enhanced dye loading on TiO$_2$ films at the current preparation condition improves performance of dye cells. Therefore, with regard to D1 devices, the deposited loosely bound dye moieties on TiO$_2$ films in D2 devices might enhance the light harvesting, thus photocurrent and $PCE$, as does the increased
loading of grafted dyes on TiO$_2$ films. To test this hypothesis, D3 devices were prepared under similar condition as D1 except that the dye concentration of the dye bath was decreased from 0.3 mM to 0.15 mM, as shown in Scheme 2. The sensitized TiO$_2$ films in D1 and D3 were all rinsed with chloroform/ethanol so that there was no loosely bound dye deposition on sensitized TiO$_2$ films. This assures that D1 and D3 devices have no deposition of loosely bound dye moieties and the latter have less grafted dye loading on the TiO$_2$ film than that in the former. As observed, D3 devices exhibit slightly higher $J_{SC}$ and PCE than D1 devices. This suggests that more grafted dye moieties on the TiO$_2$ films in D1 do not improve the solar cell performance at the current sensitization conditions of TiO$_2$ films through enhanced light harvesting. On the contrary, fewer grafted dye moieties on the TiO$_2$ films in D3 seems to alleviate dye aggregation and thus lead to higher $J_{SC}$ and PCE. Thus, we conclude that the loosely bound dye moieties in D2 behave differently from those grafted dye moieties on TiO$_2$ and are possibly contributing to the solar cell performances through other mechanisms.

It has been reported that the bulky alkoxy groups on donor end of dye molecules can effectively suppress charge recombination and improve the photovoltaic performance without influencing the charge regeneration process. Thus it reminds us that it is highly possible that the post deposition of dye moieties might provide physical insulation between TiO$_2$ film and electrolytes and thus enhance the $V_{OC}$ and $J_{SC}$. Besides, such loosely bound dye may also harvest light and contribute to the photocurrent moderately, since the charge injection efficiency to TiO$_2$ films from such loosely bound dyes may be slower than those grafted onto the TiO$_2$ films by chemical bonds.

To further corroborate that the deposition of loosely bound dye moieties on monolayer-grafted TiO$_2$ films enhance photovoltaic performances of dye cells, devices D4 were prepared with dye bath (0.15 mM dye) and ethanol rinsing, the photovoltaic performance of which were compared with devices D2 prepared with dye bath of 0.3 mM dye, as depicted in Scheme 2. We anticipated that changing the
amount of the loosely bound dyes on TiO$_2$ films may change the solar cell performance. With regard to D3, the remarkable enhancement of $V_{OC}$, $J_{SC}$ and $PCE$ was observed for D4, in accordance with the trend of performance enhancement observed in D1 and D2 devices. It is noted that D4 (0.715 V, 12.2 mA/cm$^2$, 6.2%) exhibits poorer performance than D2 (0.730 V, 12.7 mA/cm$^2$, 6.6%). As shown in Figure S4, the deposited loosely bound dye moieties on sensitized TiO$_2$ films for D2 and D4 devices could be dissolved in chloroform/ethanol solution and quantified based on the molar extinction coefficient and UV-Vis spectra of the dissolved loosely bound dye in solution, which are $4.96 \times 10^{-8}$ and $3.10 \times 10^{-8}$ moles in D2 and D4 respectively. Herein, we also need to keep in mind that the dye bath with different dye concentration not only results in different amount of loosely bound dye loading but also grafted dye moieties on TiO$_2$ films. However, as discussed above, the loading of grafted dye moieties on TiO$_2$ film does not obviously affect the performance of the solar cell under the current preparation conditions. Thus the difference of the solar cell performance between D2 and D4 devices could possibly be ascribed to the different amount of loosely bound dye moieties deposited on the sensitized TiO$_2$ films. This suggests that the solar cell performances could be tuned by changing the amount of loosely bound dye moieties on the sensitized TiO$_2$ films and further indicates that the loosely bound dye moieties dominate the difference of photovoltaic performance between D1 and D2 or D3 and D4.

In addition, if the change of photovoltaic performance between D1 and D2 or D3 and D4 is caused by deposition of loosely bound dye moieties, then removal and re-deposition of such loosely bound dyes moieties on TiO$_2$ films would restore the photovoltaic performance to its original level. However, if this change of photovoltaic performance is due to dye aggregation caused by exposure to solvent, then removal and re-deposition of such loosely bound dyes moieties on TiO$_2$ films cannot restore the
photovoltaic performance to its original level, since ethanol rinsing following the chloroform/ethanol rinse cannot restore the solar cell performance. To test this point, D5 devices were prepared by rinsing the TiO2 films sensitized in 0.3 mM dye bath with mixed ethanol/chloroform (1:1) to remove all the loosely bound dye, soaking the TiO2 films back into the 0.3 mM dye bath for 1 hour and then rinse the TiO2 films with ethanol to re-deposit loosely bound dyes on TiO2 films. It is observed that the performance of D5 (0.723 V, 12.8 mA/cm², 6.6 %) is recovered to that of D2 (0.730 V, 12.7 mA/cm², 6.6 %). The slightly lowered $V_{OC}$ in D5 with regard to D2 is possibly caused by exposure to ethanol/chloroform, leading to minimal dye aggregates. Thus this further confirms that the loosely bound dye deposition, instead of dye aggregation, caused by solvent exposure plays a dominant role in manipulating the photovoltaic performance.

One may argue that the restoration of the solar cell performance of D5 is possibly from the relaxation of dye moieties on sensitized TiO2 films while soaking in the dye bath, instead of the re-deposition of loosely bound dye moieties. To rule out the role of dye relaxation caused by solvent effect during soaking in dye bath, sensitized TiO2 films after being rinsed by ethanol/chloroform were soaked in solvent (ethanol: chloroform=4:1) without any dye sensitizers for 1 hour, and then rinsed with ethanol, and the devices prepared with these sensitized TiO2 films were denoted as D6. Under these conditions, there would be no loosely bound dye deposition but only the sensitizer relaxation if there is any on TiO2 films. As shown in Table 1, the photovoltaic performance was not restored to that of D2 at all. Instead, $V_{OC}$ and $J_{SC}$ were slightly decreased with regard to that of D1. This indicates that the soaking of sensitized TiO2 film to the mixed solvent (ethanol: chloroform=4:1) for as short as 1 hour results in minimal dye aggregation and thus deteriorates the solar cell performance. This is in agreement with that observed for D5, which exhibits slightly lowered $V_{OC}$. Comparison of D2, D5 and D6 indicates that the solvent effect on the dye aggregation upon solvent rinsing has a very limited
effect on the performance of solar cells. Thus we conclude that the change of the solar cell performance in D1 and D2 or D3 and D4 devices is most likely ascribed to the deposition of loosely bound dye moieties on sensitized TiO$_2$ films, possibly suppressing the charge recombination between e$^-$/TiO$_2$ and electrolyte.

From above discussion, we identified that deposited loosely bound dye moieties on TiO$_2$ films is the predominant factor affecting the dye cell performance and speculate that this is caused by the suppression of charge recombination between TiO$_2$ and oxidant in electrolyte. To evaluate how the deposition of the loosely bound dye moieties affects the charge recombination process and the solar cell performance, electrochemical impedance spectroscopy (EIS) was used to study the lifetime of electrons$^{24}$ in TiO$_2$ films in D1 and D2, which strongly correlate with $V_{OC}$. As shown in Figure 2, the electrochemical impedance spectra for D1 and D2 were acquired in the dark at a forward bias of -0.7 V with potential perturbation of 5 mV. The three semicircles in Nyquist plots of panel (a) are ascribed to Nernst diffusion of redox couple within electrolyte solution, charge transfer at the TiO$_2$ oxide/electrolyte interface and at the counter electrode in the order of increasing frequency from 0.1 Hz to $10^5$ Hz.$^{24,27}$ The radius of the intermediate semicircle represents the charge-transfer resistance from TiO$_2$ film to electrolyte oxidant I$_3^-$]. The smaller radius of the intermediate semicircles in D1 than D2 indicates smaller charge-transfer resistance from TiO$_2$ films to electrolyte oxidant and thus slower charge-recombination rate in the former devices than the latter. The frequency of the intermediate peak in Bode plots is 27.1 Hz and 10.2 Hz for D1 and D2. By using equation $\tau = (2\pi f)^{-1}$, where $\tau$ is the lifetime of electrons in TiO$_2$ films, $f$ is frequency of the intermediate peak in the Bode plots, the lifetimes of electrons in TiO$_2$ films are derived and it is almost 3 times longer in D2 (15.6 ms) than D1 (5.9 ms). Since the $V_{OC}$ strongly depends upon the electron concentration and Fermi level of TiO$_2$.
films, the long lived electrons in TiO$_2$ films in D2 results in higher electrons concentration and $V_{OC}$ than in D1.

However, it should be noted that, according to the diode equation describing the charge-transfer behavior, enhancement of 50 mV in $V_{OC}$ needs an almost 10-fold reduction of the charge-recombination rate.\textsuperscript{28}-\textsuperscript{30} Clearly, the 3-fold reduction of charge recombination caused by deposition of dye aggregates on TiO$_2$ film is not sufficient to change the $V_{OC}$ by 50 mV. This could possibly be correlated with formation of dipole upon charge injection of dye into the TiO$_2$ film.\textsuperscript{31,32} The amount of the loosely bound dye on TiO$_2$ films in D2 and D4 are $4.96 \times 10^{-8}$ and $3.10 \times 10^{-8}$ moles respectively. Assuming that the 10 µm transparent and 4 µm scattering layer TiO$_2$ films have surface area 1000 cm$^2$ per cm$^2$ substrate,\textsuperscript{33} the loosely bound dye have footprint of 120.6 Å$^2$ and 193.0 Å$^2$, in agreement with the reported molecular footprint of dye molecules on TiO$_2$ films.\textsuperscript{34,35} Thus, it seems that a second layer of loosely bound dye is deposited on TiO$_2$ surface on top of the first grafted dye layer. Upon charge injection of those loosely bound dye, the positive charge positions further away from TiO$_2$ surface than those grafted dye moieties, generating larger surface dipoles.\textsuperscript{23}

**Conclusion**

In conclusion, the photovoltaic performance of a D-A-$\pi$-A’ dye has been investigated in the application of DSSCs. It has been demonstrated that the open circuit voltage ($V_{OC}$), short circuit current ($J_{SC}$) and power conversion efficiency (PCE) could be remarkably enhanced by forming a loosely bound layer of the bulky dye moieties on sensitized TiO$_2$ films, which was achieved by washing the sensitized TiO$_2$ film with ethanol when being retracted from dye bath (ethanol:chloroform=4:1). Comparison experiments proved the solvent effect on the formation of dye aggregates is minimal. As demonstrated by electrochemical impedance measurements, the deposition of such loosely bound dye moieties on TiO$_2$ films could slow down the charge recombination by three
times. Thus the enhancement of photovoltaic performance of solar cells was ascribed to the retarded charge recombination between electrolyte and electrons on TiO$_2$ film, possibly due to the physical insulation of loosely bound dye between TiO$_2$ films and electrolyte redox oxidant. Furthermore, the formation of dipole upon charge injection of loosely bound dye aggregates probably also plays roles in enhancing the $V_{OC}$ of the dye cells. This study might shed light on the further design of dye sensitized TiO$_2$ films with multilayer dyes moieties, instead of monolayer, which would avoid the aggregation problem in monolayer sensitization.

**ACKNOWLEDGMENT** El-Sayed’s group would like to thank the financial support of the Office of Basic Energy Sciences of the U.S. Department of Energy under contract number DE-FG02-97ER14799 and Marder’s group would like to thank the National Science Foundation for support through the CCI Center for Selective C-H Functionalization (CHE-1205646).

Electronic Supplementary Information (ESI) available: [Experimental details for the synthesis of the dye, the cell assembly, and measurements]. See DOI: 10.1039/b000000x/
FIGURE CAPTIONS

**Scheme 1.** Synthetic route for the D–A–π–A’ dye AR-II-13

**Scheme 2.** The chart flow of diverse treatment conditions for the sensitized TiO$_2$ films

**Figure 1.** Photovoltaic performances of dye cells based on AR-II-13 sensitized TiO$_2$ film washed with CHCl$_3$/Ethanol (D1) or ethanol only (D2). The $V_{OC}$ and $J_{SC}$ for D1 is 50 mV and 2.7 mA/cm$^2$ lower than D2 respectively. The dark current onset potential for D1 and D2 is 0.45 V and 0.55 V, indicating much faster charge recombination rate for D1 than D2.

**Figure 2.** Electrochemical impedance spectra (EIS) for D1 and D2 were measured in the dark with a forward bias of -0.7 V and potential perturbation of 5 mV: (a) Nyquist plots and (b) Bode plots. The three semicircles in (a) Nyquist plots are ascribed to Nernst diffusion within electrolyte, charge transfer at the TiO$_2$ oxide/electrolyte interface and charge transfer at the counter electrode in the order of increasing frequency from 0.1 Hz to $10^5$ Hz. The frequency of the intermediate peak in Bode plots is 27.1 Hz and 10.2 Hz for D1 and D2. The electron lifetime in TiO$_2$ film could be calculated by $\tau = (2\pi f)^{-1}$, which are 5.9 ms and 15.6 ms for D1 and D2 respectively.
Notes and references

Figure 1
Figure 2
TOC

With additional weakly bound dyes

PCE = 4.9%

PCE = 6.6%
159x65mm (96 x 96 DPI)