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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

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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 TiO₂ 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 TiO₂ 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 TiO₂ films from I₃⁻ and retarding charge recombination between electrons in the TiO₂ film and the electrolyte, as confirmed by electrochemical impedance measurements. Furthermore, the dipole interaction between the TiO₂ surface and loosely bound dye may play a synergetic role in enhancing the photovoltaic performance of the resulting devices, cooperatively.

Introduction

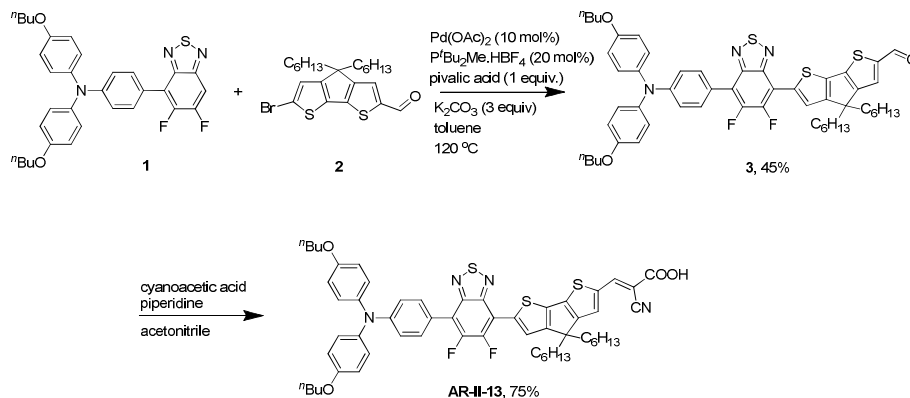
Dye sensitized solar cells (DSSCs), a type of photovoltaic devices made of transparent conductive glasses, solution-processed titanium oxide nanoparticles and organic dye molecules, have been extensively studied and developed as a promising alternative to silicon photovoltaics due to their low manufacturing cost and excellent photovoltaic performance. Since the breakthrough of power conversion efficiency (PCE) of DSSCs based on mesoporous films made of colloidal TiO₂ 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^-/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_2O_5 ,⁴ Al_2O_3 , SiO_2 , and ZrO_2 ,⁵ 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,⁸⁻¹⁰ it has been demonstrated that some sensitizers themselves could efficiently prevent charge recombination. For instance, Koumura¹¹ 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 π -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 Wang¹² 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^-/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 TiO₂ films, in some case loosely bound dyes (defined here as those easily removed by a good solvent, see below).

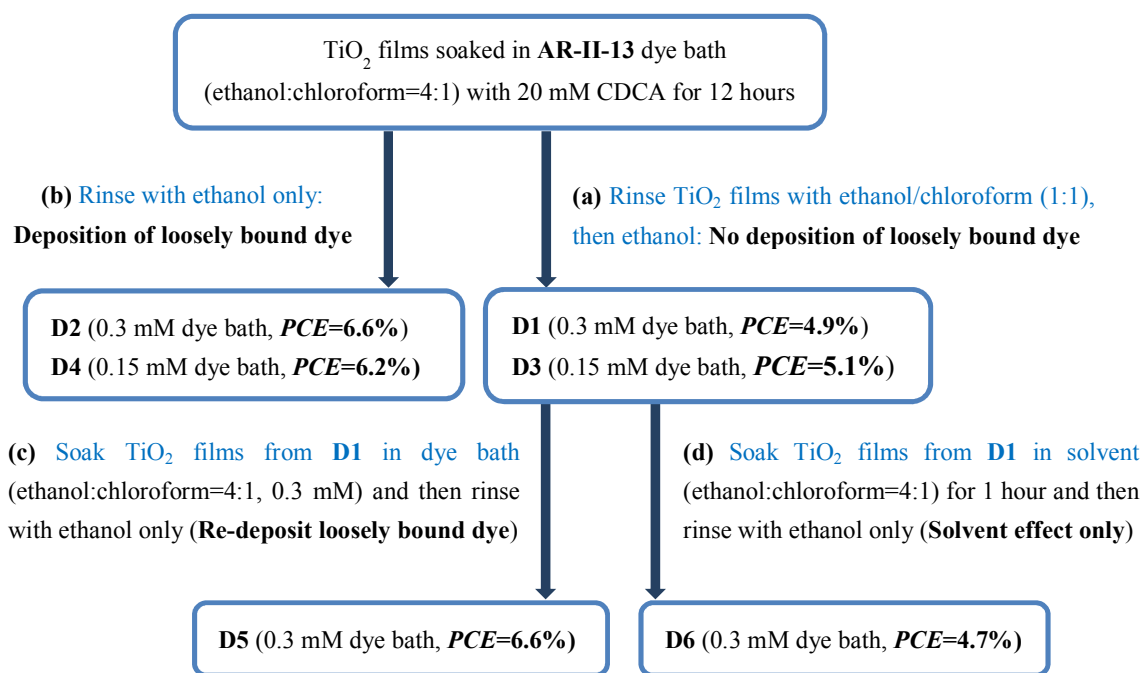
Results and Discussion

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.



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

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



Scheme 2. The chart flow of diverse treatment conditions for the sensitized TiO₂ films loosely bound dye upon the sensitized TiO₂ 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 TiO₂ film was exclusively ascribed to the suppression of charge recombination between the TiO₂ film and the electrolyte by the physical insulation offered by the loosely bound dye

moieties. This technique, to the best of our knowledge, is the first of this type that has ever been reported.

Two kinds of devices, which are denoted as **D1** and **D2**, were fabricated by the following procedures. The TiO₂ 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 TiO₂ 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 1. Photovoltaic parameters of **AR-II-13** based dye cell; TiO₂ films were sensitized in an **AR-II-13** dye bath (ethanol:chloroform=4:1) with 20 mM CDCA for 12 hours. The sensitized TiO₂ films were rinsed with **(a)** mixture of ethanol and chloroform (1:1) and then ethanol; **(b)** ethanol only; **(c)** ethanol/chloroform (1:1), then soak in dye bath for another 1 hour and then rinse with ethanol only; **(d)** ethanol/chloroform (1:1), then soak in solvent (ethanol:chloroform=4:1) for another 1 hour and then rinse with ethanol only.

	V_{OC} (V)	J_{SC} (mA/cm ²)	FF(%)	<i>PCE</i> (%)
D1, 0.3 mM ^(a)	0.681 (±0.003)	10.0 (±0.2)	71.1 (±0.2)	4.9 (±0.2)
D2, 0.3 mM ^(b)	0.730 (±0.003)	12.7 (±0.1)	71.2 (±0.8)	6.6 (±0.1)
D3, 0.15 mM ^(a)	0.680 (±0.005)	10.5 (±0.1)	71.1 (±0.6)	5.1 (±0.1)
D4, 0.15 mM ^(b)	0.715 (±0.002)	12.2 (±0.1)	71.0 (±0.1)	6.2 (±0.1)
D5, 0.3 mM ^(c)	0.723 (±0.003)	12.8 (±0.2)	70.5 (±0.5)	6.6 (±0.1)
D6, 0.3 mM ^(d)	0.671 (±0.002)	9.7 (±0.3)	72.2 (±1.4)	4.7 (±0.1)

mA/cm². In remarkable contrast, **D2** exhibits a *PCE* of 6.6%, *V*_{OC} of 0.73 V, and *J*_{SC} of 12.7 mA/cm². 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 TiO₂ 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 TiO₂ 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.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 TiO₂ 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 TiO₂ films in **D2** from dye bath solution with ethanol directly deposits loosely bound dye moieties on TiO₂ 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 TiO₂ films at the current preparation condition improves performance of dye cells. Therefore, with regard to **D1** devices, the deposited loosely bound dye moieties on TiO₂ films in **D2** devices might enhance the light harvesting, thus photocurrent and *PCE*, as does the increased

loading of grafted dyes on TiO₂ 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 TiO₂ films in **D1** and **D3** were all rinsed with chloroform/ethanol so that there was no loosely bound dye deposition on sensitized TiO₂ 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 TiO₂ 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 TiO₂ films in **D1** do not improve the solar cell performance at the current sensitization conditions of TiO₂ films through enhanced light harvesting. On the contrary, fewer grafted dye moieties on the TiO₂ 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 TiO₂ 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.²⁰ Thus it reminds us that it is highly possible that the post deposition of dye moieties might provide physical insulation between TiO₂ 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 TiO₂ films from such loosely bound dyes may be slower than those grafted onto the TiO₂ films by chemical bonds.²¹⁻²³

To further corroborate that the deposition of loosely bound dye moieties on monolayer-grafted TiO₂ 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 TiO₂ 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/cm², 6.2%) exhibits poorer performance than **D2** (0.730 V, 12.7 mA/cm², 6.6%). As shown in **Figure S4**, the deposited loosely bound dye moieties on sensitized TiO₂ 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 4.96×10^{-8} and 3.10×10^{-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 TiO₂ films. However, as discussed above, the loading of grafted dye moieties on TiO₂ 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 TiO₂ films. This suggests that the solar cell performances could be tuned by changing the amount of loosely bound dye moieties on the sensitized TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ films, possibly suppressing the charge recombination between e⁻/TiO₂ and electrolyte.

From above discussion, we identified that deposited loosely bound dye moieties on TiO₂ films is the predominant factor affecting the dye cell performance and speculate that this is caused by the suppression of charge recombination between TiO₂ 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 electrons²⁴⁻²⁶ in TiO₂ 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 TiO₂ oxide/electrolyte interface and at the counter electrode in the order of increasing frequency from 0.1 Hz to 10⁵ Hz.^{24,27} The radius of the intermediate semicircle represents the charge-transfer resistance from TiO₂ film to electrolyte oxidant I₃⁻. The smaller radius of the intermediate semicircles in **D1** than **D2** indicates smaller charge-transfer resistance from TiO₂ 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 τ is the lifetime of electrons in TiO₂ films, f is frequency of the intermediate peak in the Bode plots, the lifetimes of electrons in TiO₂ 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 TiO₂

films, the long lived electrons in TiO₂ 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.²⁸⁻³⁰ Clearly, the 3-fold reduction of charge recombination caused by deposition of dye aggregates on TiO₂ 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 TiO₂ film.^{31,32} The amount of the loosely bound dye on TiO₂ films in **D2** and **D4** are 4.96×10^{-8} and 3.10×10^{-8} moles respectively. Assuming that the 10 μm transparent and 4 μm scattering layer TiO₂ films have surface area 1000 cm² per cm² substrate,³³ the loosely bound dye have footprint of 120.6 Å² and 193.0 Å², in agreement with the reported molecular footprint of dye molecules on TiO₂ films.^{34,35} Thus, it seems that a second layer of loosely bound dye is deposited on TiO₂ surface on top of the first grafted dye layer. Upon charge injection of those loosely bound dye, the positive charge positions further away from TiO₂ surface than those grafted dye moieties, generating larger surface dipoles.²³

Conclusion

In conclusion, the photovoltaic performance of a D-A- π -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 TiO₂ films, which was achieved by washing the sensitized TiO₂ 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 TiO₂ 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 TiO₂ film, possibly due to the physical insulation of loosely bound dye between TiO₂ 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 TiO₂ films with multilayer dyes moieties, instead of monolayer, which would avoid the aggregation problem in monolayer sensitization.

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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 TiO₂ films

Figure 1. Photovoltaic performances of dye cells based on **AR-II-13** sensitized TiO₂ film washed with CHCl₃/Ethanol (**D1**) or ethanol only (**D2**). The V_{OC} and J_{SC} for **D1** is 50 mV and 2.7 mA/cm² 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 TiO₂ oxide/electrolyte interface and charge transfer at the counter electrode in the order of increasing frequency from 0.1 Hz to 10⁵ 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 TiO₂ film could be calculated by $\tau = (2\pi f)^{-1}$, which are 5.9 ms and 15.6 ms for **D1** and **D2** respectively.

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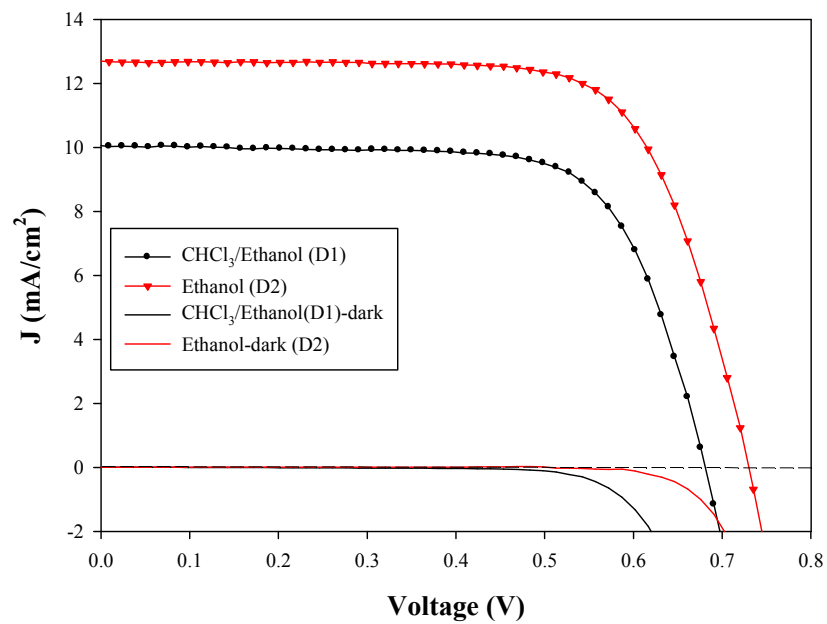


Figure 1

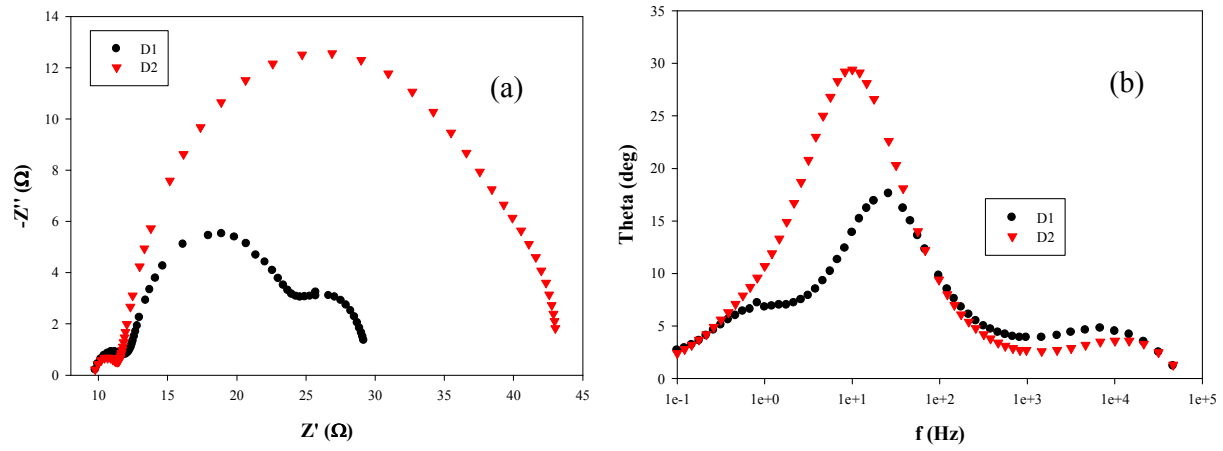
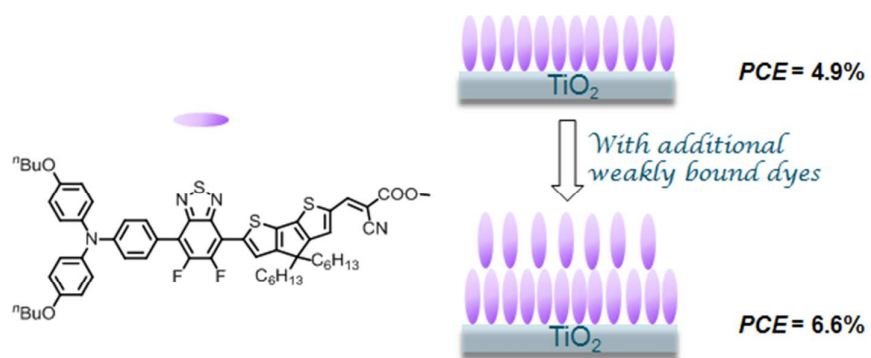
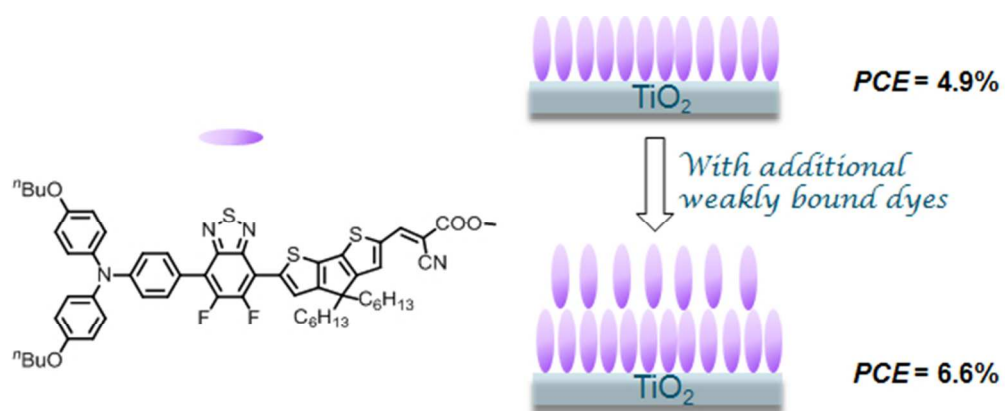


Figure 2

TOC





159x65mm (96 x 96 DPI)