

## Research Article

# Improving the Spectral Response of Black Dye by Cosensitization with a Simple Indoline Based Dye in Dye-Sensitized Solar Cell

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Indoline dye **D-1** was successfully applied as a cosensitizer for improving the spectral response of black dye in dye-sensitized solar cells (DSCs). It was observed that **D-1** effectively increases the short-circuit photocurrent by offsetting the competitive light absorption by  $I^-/I_3^-$  electrolyte in the wavelength region 350–500 nm when adsorbed on the  $TiO_2$  nanocrystalline films in a mix dye system. The DSCs containing the **D-1** and black dye achieved a power conversion efficiency of 9.80% with higher short-circuit photocurrent of 19.54 mA/cm<sup>2</sup> compared to the system of black dye without cosensitization under standard AM 1.5 sunlight.

## 1. Introduction

Dye-sensitized solar cells (DSSC) based on nanocrystalline  $TiO_2$  electrodes are promising candidate for low-cost alternative energy sources compared to silicon and other inorganic semiconductor-based photovoltaic devices [1–5]. Therefore, many researchers have continued their tremendous efforts over the last two decades for improving the performances of DSCs [6–9]. In DSCs, a sensitizing dye adsorbed at the surface of a wide band gap semiconductor (usually nanostructured  $TiO_2$ ) absorbs light to transfer an electron to the semiconductor conduction band, followed by dye regeneration by a solution redox electrolyte or a solid hole conductor. The most common and efficient dyes employed so far in these solar cells are Ru(II) polypyridyl complexes as their intense charge-transfer (CT) absorption in the whole visible range, high quantum yield for the formation of the lowest CT excited state, and ease to tune redox properties [10–18]. The photoexcitation of the metal-to-ligand charge-transfer (MLCT) excited states of the adsorbed dye leads to an efficient injection of electrons into the conduction band

of  $TiO_2$ . Up to now, the highest conversion efficiency ( $\eta$ ) from solar light to electric power for DSCs is over 11% under standard AM 1.5 conditions, which has been obtained from porous  $TiO_2$  electrode using Ru polypyridine complexes (black dye) as sensitizers, and an organic electrolyte containing  $I^-/I_3^-$  as a hole transport media [7]. However, the conversion efficiency of DSCs is still lower than that of the silicon-based photovoltaic cells. It will be required to improve the light harvesting efficiency in the near-IR region as well as over the entire visible region of the solar spectrum to further improve the conversion efficiency. Black dye based DSCs show a strong dip at about 380 nm in the incident photon-to-current conversion efficiency (IPCE) spectrum due to the competitive light absorption of the triiodide and black dye. To overcome this problem, recently a mix dyes system has been used to avoid the competitive adsorption and aggregation among dyes that may induce unfavorable charge or energy transfer and quenching of photo-excited states [8, 9]. Although the efficiency of black dye increased with the combination of an organic dye, the mechanism and selection of this dye in that system has yet to be clear.

To understand this system and effectiveness, here, we have strategically chosen dye **D-1** (Figure 1) as a cosensitizer considering its strong light harvesting efficiency at around 400 nm and also studied its performance with the black dye in mix dye-sensitized DSCs.

## 2. Experimental Section

All reagents were purchased from Sigma-Aldrich and Alfa Aesar. The dye **D-1** was synthesized according to the published method [19]. Absorption spectra were recorded on a Shimadzu model 3100 UV-Vis-NIR spectrophotometer. Nanocrystalline TiO<sub>2</sub> films were prepared by using a variation of a reported method [20]. TCO glass electrodes with a sheet resistance of 8–10 ohm<sup>-2</sup> and an optical transmission of greater than 80% in the visible range were used. A double-layer TiO<sub>2</sub> photoelectrode (15 + 5) μm in thickness with a 15 μm thick nanoporous layer and a 5 μm thick scattering layer (area: 0.25 cm<sup>2</sup>) was prepared by screen printing on a conducting glass substrate. The films were then sintered at 500°C for 1 hour. The thickness of films was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The films were further treated with 0.1 M HCl aqueous solutions before examination [21]. A mixture of black dye (tri(thiocyanato)(4,4',4''-tricarboxy-2,2':6',2''-terpyridine)ruthenium(II)) (0.2 mM) and **D-1** (0.1 mM) with addition of deoxycholic acid at a concentration of 20 mM in 1:1 acetonitrile and tert-butanol was used as a mix dye solution. The TiO<sub>2</sub> films were immersed in the above solutions and then kept at 25°C for 30 hours. The dye deposited TiO<sub>2</sub> film and a platinum-coated conducting glass were separated by a Surlyn spacer (40 mm thick) and sealed by heating the polymer frame. An electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide, 0.05 M I<sub>2</sub>, 0.1 M LiI, and 0.4 M tert-butylpyridine in acetonitrile was used in all the cells.

The current-voltage characteristics were measured using a black metal mask with an aperture area of 0.25 cm<sup>2</sup> under standard air mass 1.5 sunlight (100 mW cm<sup>-2</sup>). Monochromatic incident photon-to-current conversion efficiency spectra were measured with a monochromatic incident light of 1 × 10<sup>16</sup> photons cm<sup>-2</sup> in direct current mode (CEP-2000BX). The photoemission yield curves were measured with an AC-3 photoelectron spectrometer surface analyzer under atmosphere with a 0.2 mL min<sup>-1</sup> N<sub>2</sub> flow.

## 3. Results and Discussions

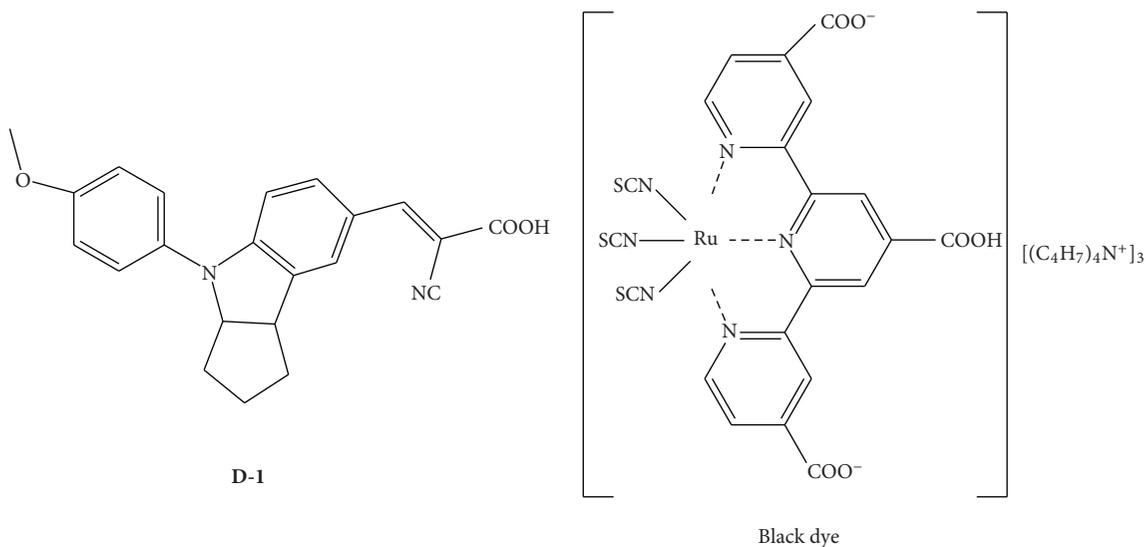
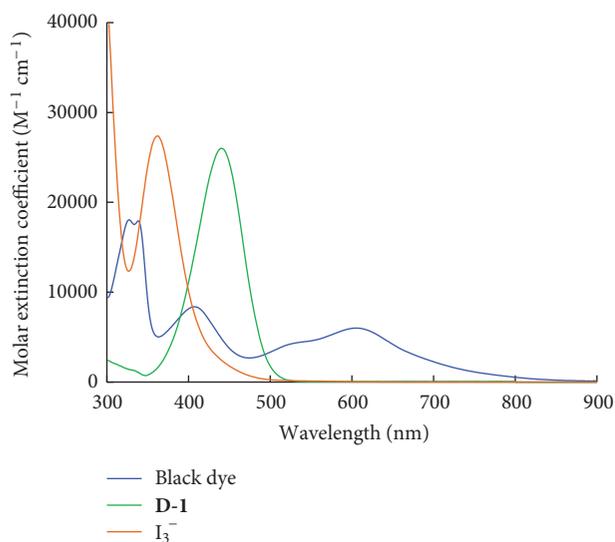
Figure 2 shows the UV-visible absorption spectra of black dye, **D-1**, and triiodide in ethanol solutions. The cosensitizer **D-1** showed strong absorptions near 440 nm with a high molar extinction coefficient ( $\epsilon$ ) of  $2.53 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . We assigned this absorption to the intramolecular charge transfer between the donors and the acceptors in **D-1**. The broad and intense visible bands of black dye in the 390–540 nm region are due to the metal-to-ligand charge transfer transitions. As shown in Figure 2, **D-1** shows a superior light harvesting efficiency in the wavelength region of 400–500 nm compared

to that of black dye and I<sub>3</sub><sup>-</sup>. Compared to the molar extinction coefficients of I<sub>3</sub><sup>-</sup>, **D-1** showed much higher light harvesting ability in this region which may attribute to the loss of the light absorption by I<sub>3</sub><sup>-</sup> to be suppressed by the use of cosensitizer **D-1**.

Figure 3 shows the absorption spectra of black dye, **D-1**, and a mixture of black dye and **D-1** absorbed on transparent thin film of nanoporous TiO<sub>2</sub> (4 μm). Both **D-1** and black dye showed broad absorption spectra similar to that in solution. However, the absorption maxima were slightly blue-shifted due to the interaction between the carboxylate group and TiO<sub>2</sub> (Figure 3). Upon adsorption on TiO<sub>2</sub> film, the tail of the absorption spectra of black dye and **D-1** extended to 600 nm and 850 nm, respectively. This broadening of the absorption spectra is desirable for harvesting the solar spectrum and leads to a higher photocurrent. The electronic absorption spectrum of **D-1** adsorbed on TiO<sub>2</sub> shows a well defined intense absorption band at around 430 nm. The absorbance of this band is much higher than that for black dye at this wavelength. The absorption spectrum of mix dye (BD + **D-1**) coated transparent TiO<sub>2</sub> film shows a broad absorption band ranging from 340–650 nm. As shown in Figure 3, it is clear that mix dye system shows superior light harvesting efficiency than black dye in the wavelength region 360–540 nm. Therefore it is expected that mix dye sensitized DSCs show better incident photon-to-electron conversion efficiency (IPCE) compared to black dye based DSCs in 360–540 nm and also improve the dip at about 400 nm in the IPCE spectrum of black dye based DSCs due to the competitive light absorption of the triiodide ion.

The ionization potential (IP) of **D-1** bound to nanocrystalline TiO<sub>2</sub> film was determined by using the photoemission yield spectrometer. Ground-state oxidation potential (HOMO) values of -6.11 eV was obtained for sensitizers **D-1**. The HOMO energy level of **D-1** was sufficiently low compared to the redox potential of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> (-5.20 eV) for efficient regeneration of oxidized dye through reaction with iodide. The onset of the optical energy gap ( $E_{0-0}$ ) of **D-1** was 2.38. The excited-state oxidation potential, LUMO, of sensitizer **D-1** was -3.73 eV, which lies above the conduction band edge (-4.2 eV) of the nanocrystalline TiO<sub>2</sub>. Therefore, an efficient electron injection into the conduction band of TiO<sub>2</sub> is expected to occur for sensitizer **D-1**.

Figure 4 shows the monochromatic incident photon to current conversion efficiency for DSCs based on black dye, **D-1**, and a mixture of black dye and **D-1**. The dye **D-1** shows excellent sensitization of nanocrystalline TiO<sub>2</sub> from 400 to 550 nm with a maximum value of 85% in the plateau region. Taking into account the reflection and absorption losses by the conducting glass, the photon to current conversion efficiency in this range reaches about 95%. The IPCEs of **D-1** in 370–510 nm are high in comparison with that of **black dye**. The cell with only black dye showed a broad IPCE spectrum extending across the whole visible range and into the near-IR region as far as 950 nm and displayed the highest IPCE value (73%) in the wavelength range from 600 to 700 nm (Figure 4). The IPCE, in the wavelength range 350–450 nm, was decreased due to competitive light absorption between I<sub>3</sub><sup>-</sup> and the black dye. Addition of

FIGURE 1: Chemical structure of dye **D-1** and black dye.FIGURE 2: UV-visible absorption spectra of black dye, **D-1**, and triiodide in ethanol solutions.

cosensitizer **D-1** for the cell with black dye enhanced the IPCE in the wavelength range 350–600 nm. The dip in the IPCE spectra at around 400 nm was restored as shown in Figure 4 by adding the cosensitizer **D-1** into the cells which indicates that the electron could easily inject from the **D-1** into the  $TiO_2$  film in the mix dye sensitized DSCs. This result was consistent with the absorption spectrum of **D-1**. The IPCE spectra of black dye and mix dye sensitized DSCs were almost the same in the wavelength range 600–950 nm which indicates that both black dye and **D-1** work independently with negligible interaction.

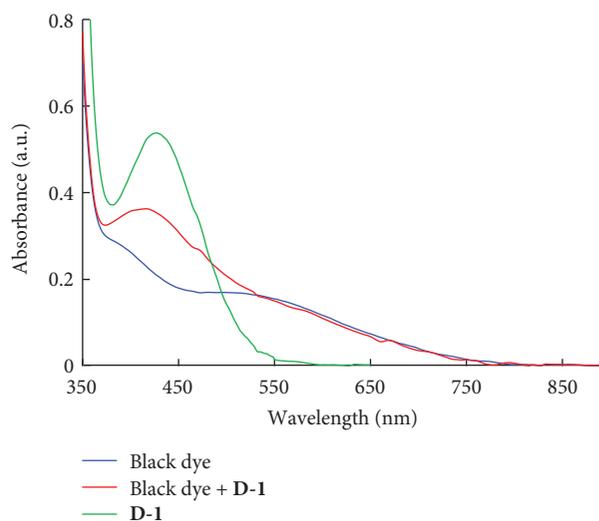
FIGURE 3: UV-visible absorption spectra of black dye, **D-1**, and black dye + **D-1** (mix-dye) on  $TiO_2$  film.

Figure 5 shows the  $I-V$  curves for DSCs based on black dye, **D-1**, and a mixture of black dye and **D-1**. The short-circuit photocurrent density, open-circuit voltage, fill factors, and overall cell efficiencies for DSCs are summarized in Table 1. The **mix dye** sensitized solar cell showed higher power conversion efficiency than **black dye**, with  $J_{sc}$  of  $19.54 \text{ mA cm}^{-2}$ ,  $V_{oc}$  of 0.703 V, FF of 0.714, and corresponding to an overall conversion efficiency ( $\eta$ ) of **9.80%**. Under the same conditions, **black dye** showed a  $J_{sc}$  of  $18.15 \text{ mA cm}^{-2}$ ,  $V_{oc}$  of 0.704 V, FF of 0.719, and an overall conversion efficiency ( $\eta$ ) of **9.18%**. The improved photocurrent of **mix dye** sensitized solar cell relative to **D-1** is in good accord with the preceding IPCE measurements.

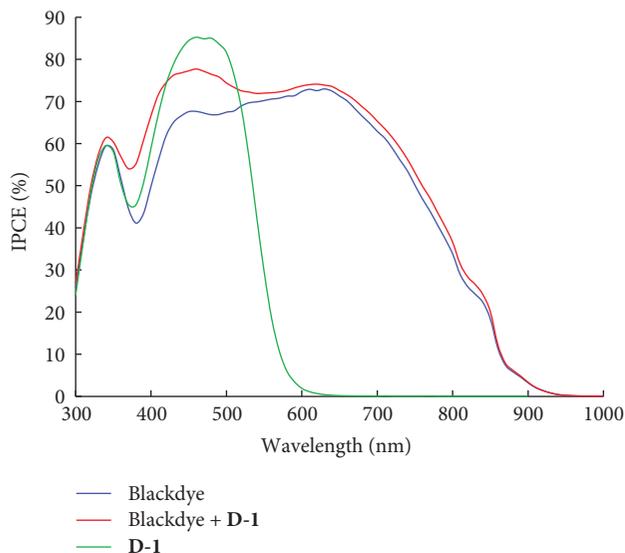


FIGURE 4: Incident photon-to-electron conversion efficiency (IPCE) spectra of DSCs.

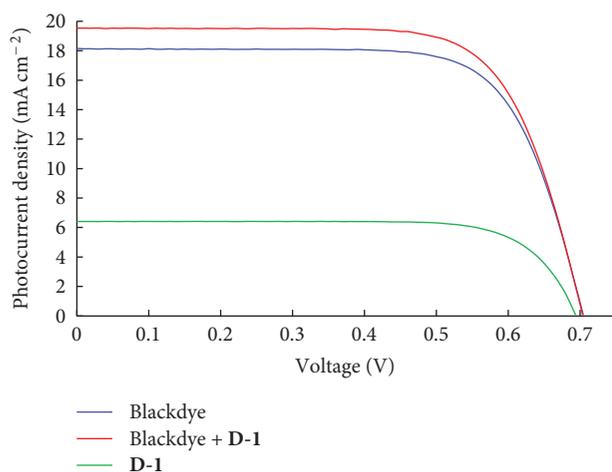


FIGURE 5: Current-voltage characteristics of the DSCs under AM1.5 sunlight illumination ( $100 \text{ mW cm}^{-2}$ ).

TABLE 1: The current-voltage performance data of DSCs sensitized by black dye, **D-1**, and black dye + **D-1** (mix-dye) measured AM1.5 sunlight illumination ( $100 \text{ mW cm}^{-2}$ ).

Compound	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	$V_{oc}$ (V)	FF	Eff. (%)
<b>D-1</b>	6.420	0.705	0.750	3.34
Black-dye	18.150	0.704	0.719	9.18
Black-dye + <b>D-1</b>	19.540	0.703	0.714	9.80

#### 4. Conclusion

The combination of black dye and **D-1** was found to exhibit improvement of cell efficiency by offsetting the competitive visible light absorption due to  $\text{I}_3^-$ . Addition of **D-1** as a cosensitizer in the mix dye based DSC shows an enhanced IPCE in the wavelength range of 350–600 nm leading to an

improved photocurrent. The distinct properties of **D-1** as a cosensitizer enabled mix dye based DSCs to perform with high efficiency.

#### Acknowledgment

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