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Triazatruxene-based organic dyes containing a rhodanine-3-acetic acid acceptor for dye-sensitized solar cells



PIGMENTS

Xing Qian, Lin Lu, Yi-Zhou Zhu^{*}, Huan-Huan Gao, Jian-Yu Zheng^{*}

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

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ABSTRACT

Two novel triazatruxene-based organic dyes with a rhodanine acceptor have been designed, synthesized, and applied as photosensitizers for dye-sensitized solar cells. The photophysical and electrochemical properties of the dyes were investigated using UV–vis absorption spectroscopy, electrochemistry, and density functional theory calculations. Dyes with π -conjugated spacers, thiophene and benzene, both showed broad IPCE responses even up to 800 nm which covers almost the whole visible light spectrum and offers great potential in DSSCs. An overall conversion efficiency of 3.60% under AM 1.5 illumination (100 mW cm⁻²) was achieved with the benzene spaced dye.

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1. Introduction

Solar energy application has been considered as a powerful alternative to petroleum and coal and has attracted increasing attention because of the fossil fuel depleting. As a low-cost device for solar energy-to-electricity conversion, dye-sensitized solar cells (DSSCs) have been extensively explored [1,2]. In DSSCs, the sensitizer is the crucial component for better light harvesting and high conversion efficiency [3]. Recently, metal-free organic sensitizers have been widely investigated for their structural diversity, high molar extinction coefficient, facile synthesis, low cost, and environmentally friendly characteristics [4].

Most of the organic sensitizers for DSSCs are characterized by an electron donor, a π -conjugated bridge, and an electron acceptor (D- π -A) [5]. Triazatruxene (TAT), owing to its unique discotic π -extended and electron-rich aromatic structure, has been used to produce various functional materials [6]. Benefiting from its strong intramolecular charge transfer characteristic, synthetic flexibility, and high stability, novel triazatruxene-based sensitizers were

recently designed and synthesized for dye-sensitized solar cells in our group [7].

Generally, organic dyes are required to possess broad and intense spectral absorption in the visible light region for achieving high conversion efficiency [8]. Electron acceptor units also have significant influence on the photo-electronic properties because the excited electrons from the dye molecules are injected to the semiconductor film through the acceptor units [9]. To induce intramolecular charge transfer (ICT) from donor to acceptor efficiently, an electron-deficient acceptor is essential [10]. Rhodanine-3-acetic acid, due to its strong electron-withdrawing ability, has been used as an efficient electron acceptor in a series of organic dyes. For example, indoline-based dye D149 (Fig. 1) with rhodanine-3-acetic acid as the acceptor gave power conversion efficiency (PCE) of 9.03% [11]. Another indoline dye D205 (Fig. 1) was designed by introducing a *n*-octyl group onto the rhodanine ring of D149, and exhibited a PCE value of 9.52%, using an antiaggregation reagent (chenodeoxycholic acid), which is the highest efficiency obtained among DSSCs based on indoline-based dyes [12]. Based on these studies, we report here the synthesis, structural characterization, and investigation of the electrochemical, photophysical, and photovoltaic properties of two novel organic dyes based on triazatruxene (5,10,15-triethyl-10,15-



^{*} Corresponding authors. Tel./fax: +86 22 2350 5572.

E-mail addresses: zhuyizhou@nankai.edu.cn (Y.-Z. Zhu), jyzheng@nankai.edu.cn (J.-Y. Zheng).



Fig. 1. Chemical structures of D149, D205, JY04, and JY05.

dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole) framework containing a rhodanine-3-acetic acid. Thiophene and benzene were applied as the π -conjugated linkers, and the resultant molecular structures are shown in Fig. 1.

2. Experimental

2.1. Materials and instruments

All NMR solvents were used as received. ¹H NMR and ¹³C NMR spectra were recorded on Bruker 400 MHz spectrometer using TMS as internal standard. Cyclic voltammetry experiments were carried out with a conventional three-electrode system employing glassy carbon electrode as working electrode, Ag/Ag⁺ electrode as reference electrode, and Pt wire as counter electrode. The redox potentials were measured in dichloromethane, using 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte with a scan rate of 100 mV S⁻¹. IR spectra were recorded from KBr disk on the Bruker Tensor 27. All other chemicals were used as received without further purification. All solvents were purified according to standard methods.

2.2. Fabrication and characterization of DSSCs

A TiO₂ film (thickness, ~10 μ m) was prepared according to the doctor-blade method by coating a commercial TiO₂ sol (particle size, 20 nm, China National Academy of Nanotechnology & Engineering) onto the pre-treated FTO glass (Nippon Sheet Glass, Japan, fluorine-doped SnO₂ over layer, sheet resistance of 15 Ω /sq). A scattering layer (thickness, ~4 μ m, particle size, 200 nm) was then applied over the transparent layer, and the film was calcined at 500 °C for 60 min in a Muffle furnace at air. The resulting TiO₂ electrodes were treated by 40 mM TiCl₄ solution for 1 h at 70 °C and sintered again at 500 °C for 60 min. The active area of cells is 0.16 cm². The Pt electrode was obtained by thermal deposition a platinum layer on the surface of FTO at 450 °C for 30 min. The TiO₂ photoanodes were immersed in commercial N719 dye solution

(0.3 mM in ethanol) for 24 h. The adsorption of the triazatruxenebased dyes on TiO₂ was carried out with 0.3 mM dye solution in tetrahydrofuran for 12 h. Chenodeoxycholic acid (CDCA) (10 mM) as a coadsorbent was added into the dye solution to prevent the aggregation of dye molecules on the surface of TiO₂. The electrolyte was composed of 0.3 M DMPII, 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-tertbutylpyridine in acetonitrile. The DSSCs were illuminated by a solar simulator (Oriel[®] Sol2A, 94022A, Newport Corporation) under 100 mW/cm² irradiation, which was calibrated by a standard silicon solar cell (91150V, Newport Corporation). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). The photocurrent intensity-voltage (J-V) characteristic curves of the DSSC under simulated sunlight were recorded using an IM6ex electrochemical workstation (Zahner, Germany).

2.3. Dye synthesis

The synthetic routes of the sensitizers **JY04** and **JY05** are shown in Scheme 1. Target dyes were synthesized from isatin by five reaction steps. The intermediates **2**, **3**, and **4** were prepared according to literature procedures [13]. Bromination and subsequent Suzukicoupling of compound **4** produced the π -extended triazatruxene bearing aldehydes **5** and **6**. Knoevenagel reaction of the resulting aldehydes and cyanoacetic acid afforded the target sensitizers **JY04** and **JY05**.

2.3.1. Synthesis of compound 5

A solution of *N*-bromosuccinimide (NBS) (166 mg, 0.93 mmol) in DMF (5 mL) was added dropwise to the chloroform (30 mL) solution containing compound **4** (400 mg, 0.93 mmol) at 0 °C. Then the mixture was slowly warmed to room temperature and stirred for 1 h before it was poured into water. The organic phase was separated and dried over anhydrous Na₂SO₄. After the solvent was evaporated, the crude product was transferred into a two-neck round bottomed flask. 5-Formylthiophene-2-boronic acid (284 mg, 1.82 mmol), Pd(PPh₃)₄ (53 mg, 0.045 mmol), aqueous 2 M Na₂CO₃ (7 mL), toluene (15 mL), and ethanol (5 mL) were successively added. The flask was charged with N₂. The mixture was heated under reflux for 5 h before it was poured into water. Then,



Scheme 1. Synthetic procedures for triazatruxene-based dyes.

the organic phase was separated and dried over anhydrous Na₂SO₄. After the solvent was removed under vacuum, the crude product was purified by silica-gel column chromatography using CH₂Cl₂/ petroleum ether (1:1) as the eluent to afford compound **5** as an orange solid (Yield: 36.4%). IR (KBr): 3043, 2968, 2929, 1658, 1608, 1564,1435, 1331, 1225, 729 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 8.33 (dd, *J* = 15.0, 7.9 Hz, 3H), 7.89 (s, 1H), 7.77 (t, *J* = 9.1 Hz, 1H), 7.66 (dd, *J* = 11.6, 4.7 Hz, 3H), 7.56–7.43 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 5.12–4.92 (m, 6H), 1.68–1.57 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 182.71, 155.81, 141.57, 140.86, 140.73, 140.65, 139.65, 139.09, 138.24, 137.81, 127.40, 124.58, 123.41, 123.29, 123.14, 121.76, 121.59, 121.49, 120.11, 120.05, 118.44, 110.44, 110.37, 107.80, 103.53, 103.13, 103.09, 41.71, 41.64, 15.60, 15.57. HR-MS (MALDI): m/z [M]⁺ calcd for C₃₅H₂₉N₃OS 539.2031; found, 539.2028.

2.3.2. Synthesis of compound 6

The synthesis resembles that of compound **5** using 4-formylphenylboronic acid instead of 5-formylthiophene-2-boronic acid. Purification by silica-gel column chromatography with CH₂Cl₂/petroleum ether (1:1) as the eluent afforded compound **6** as a yellow solid (Yield: 48.3%). IR (KBr): 3050, 2972, 2933, 1702, 1600, 1562, 1332, 1227, 730 cm^{-1.} ¹H NMR (400 MHz, CDCl₃) δ 10.09 (s, 1H), 8.46–8.29 (m, 3H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.88 (s, 1H), 7.76–7.58 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 5.19–4.90 (m, 6H), 1.76–1.58 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 192.03, 147.89, 141.25, 140.78, 140.69, 139.46, 138.96, 138.42, 134.79, 134.13, 130.40, 127.71, 123.83, 123.40, 123.09, 121.84, 121.59, 121.51, 120.04, 120.01, 119.36, 110.44, 110.35, 108.81, 103.46, 103.22, 102.99, 41.73, 41.66, 15.65, 15.61. HR-MS (MALDI): m/z [M]⁺ calcd for C₃₇H₃₁N₃O, 533.2467; found, 533.2467.

2.3.3. Synthesis of JY04

A mixture of compound 5 (40 mg, 0.074 mmol), ammonium acetate (28 mg, 0.37 mmol), rhodanine-3-acetic acid (17 mg, 0.09 mmol), and acetic acid (5 mL) was heated at reflux for 3 h under a nitrogen atmosphere. After cooling to room temperature, it was precipitated by pouring into water. The resulting solid was filtered, washed thoroughly with water. Then, the crude product was purified by silica-gel column chromatography using CH₂Cl₂/ CH₃OH (10:3) as the eluent to afford **JY04** as a dark red solid (Yield: 83.5%). IR (KBr): 3057, 2976, 2928, 1707, 1579, 1426, 1332, 1202, 744 cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆) δ 8.43-8.28 (m, 3H), 8.24-8.16 (m, 1H), 8.15-8.03 (m, 1H), 7.97 (s, 1H), 7.91-7.71 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 12.2, 7.4 Hz, 2H), 5.26–4.86 (m, 6H), 4.69 (s, 2H), 1.68–1.35 (m, 9H). ¹³C NMR (101 MHz, DMSO) δ 191.73, 167.22, 165.85, 153.76, 140.34, 140.16, 140.04, 138.72, 138.28, 138.14, 137.27, 135.51, 127.09, 126.88, 125.38, 123.22, 122.30, 122.19, 121.79, 121.30, 121.25, 120.26, 120.15, 118.43, 117.60, 110.83, 110.70, 107.49, 102.66, 102.50, 102.42, 45.00, 41.11, 15.28, 15.24, 15.09. HR-MS (ESI): m/z [M–H]⁻ calcd for C₄₀H₃₁N₄O₃S₃, 711.1558; found, 711.1573.

2.3.4. Synthesis of JY05

The synthesis resembles that of **JY04** using intermediate **6** instead of compound **5**. The compound was purified by silica-gel column chromatography using CH₂Cl₂/CH₃OH (10:3) as the eluent to afford compound **JY05** as a red solid (Yield: 82.0%). IR (KBr): 3056, 2969, 2931, 1718, 1586, 1476, 1332, 1203, 728 cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.35 (t, *J* = 8.0 Hz, 2H), 8.23 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.96 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.80 (t, *J* = 8.2 Hz, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (dt, *J* = 10.9, 5.5 Hz, 2H), 5.14 (d, *J* = 6.9 Hz, 2H), 5.09–4.98 (m, 4H), 4.74 (s, 2H), 1.70–1.35 (m, 9H). ¹³C NMR (101 MHz, DMSO) δ 192.96, 167.19, 166.33, 143.13, 140.69, 140.15, 140.04, 138.46, 137.94, 137.43, 133.61, 133.26, 131.51, 131.26, 130.70, 127.66, 123.15, 122.58, 122.36,

122.29, 121.71, 121.32, 121.29, 121.22, 120.94, 120.59, 120.19, 120.12, 119.02, 110.80, 110.71, 108.81, 102.57, 102.43, 102.27, 45.04, 41.13, 41.08, 15.25, 15.17, 15.09. HR-MS (ESI): m/z $[M-H]^-$ calcd for $C_{42}H_{33}N_4O_3S_2$, 705.1994; found, 705.1994.

3. Results and discussion

3.1. UV-visible absorption and electrochemical characterization

The UV-vis absorption spectra of the two dyes in THF solutions and on TiO₂ films are depicted in Fig. 2. Data of absorption, electrochemical properties, and frontier orbital energy levels are summarized in Table 1. In THF solutions, each of these organic dyes exhibited two major absorption bands at 300-350 and 400-600 nm. The high-energy absorption bands ranging from 300 to 350 nm correspond to the $\pi - \pi^*$ transition of the conjugated aromatic rings. The low-energy bands appearing at 400-600 nm with weaker intensity can be attributed to the intramolecular charge transfer (ICT) transitions [14]. The peak at 507 nm of JY04 is red-shifted in comparison to that of JY05 (456 nm) due to the relatively more electron-rich thiophene unit, which enhanced the interaction between the donor and acceptor. The molar extinction coefficients at λ_{max} of **JY04** and **JY05** are 38355 and 34851 M⁻¹ cm⁻¹, respectively. These are more than twice as high as those of conventional polypyridyl Ru(II) complexes dyes, which is conducive to increase the light harvesting of the cells [15]. As shown in Fig. 2, when anchoring on mesoporous TiO₂ films, both



Fig. 2. UV-vis absorption spectra of the dyes (a) in THF solutions and (b) on TiO₂ films.

lable I		
Photophysical and	electrochemical	data of the dyes.

Dye	λ_{max}^{a}/nm	$\epsilon/M^{-1}cm^{-1a}$	$E_{\rm ox}/V^{\rm b}$	E_{0-0}/V^c	$E_{\rm red}/V^{\rm d}$	HOMO/LUMO/eV ^e
JY04	320	62,919	0.89	1.91	-1.02	-5.39/-3.48
JY05	319	77,220	0.90	2.06	-1.16	-5.40/-3.34
	456	34,851				

^a The absorption spectra were measured in THF solutions.

^b First oxidation potentials (vs. NHE) in CH₂Cl₂ were internally calibrated with ferrocene (0.63 V vs. NHE).

 $^{\rm c}$ E_{0-0} values (zeroth-zeroth transition energies) were estimated from the onset wavelength in absorption spectra in THF.

 $E_{red} = E_{ox} - E_{0-0}$.

^e NHE vs. the vacuum level was set to 4.5 V.

JY04 and **JY05** show significantly broadened absorption spectra compared to that measured in THF solutions. The absorption maxima of the dyes on TiO_2 were similarly ranked as those of the dyes in THF solutions.

Cyclic voltammetry measurements were used to study the redox behavior of the dyes in CH₂Cl₂, using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The HOMO levels of the two dyes correspond to the first oxidation potential versus normal hydrogen electrode (NHE) calibrated against Fc/Fc⁺ (0.63 V vs. NHE) [16]. The LUMO levels could be calculated from $E_{\text{ox}} - E_{0-0}$, where E_{0-0} is the zeroth–zeroth energy of the dye estimated from the onset wavelength in absorption spectra in THF. The oxidation potential of the two dyes could be determined from the peak potentials. As shown in Table 1, the oxidation potential of the two dyes show a first reversible oxidation wave at 0.89 (**JY04**) and 0.90 V (**JY05**), respectively. The HOMO levels of the two dyes are evaluated to be higher than the redox potential of the iodide/ triiodide redox couple (0.4 V vs NHE), which guarantees efficient dye regeneration. On the other hand, the LUMO levels of the two dyes (-1.02 and -1.16 V vs. NHE, respectively) are both more negative than the conduction band (CB) of TiO₂ (-0.5 V vs NHE) allowing efficient electron injection from the excited dyes into the TiO₂ electrode.

3.2. Theoretical calculations

To gain a further insight into the geometrical and electronic properties of the studied dyes, theoretical calculations were conducted by density functional theory (DFT) using the Gaussian 03 program package at the B3LYP/6-31G(d) level. Fig. 3 displays the relative energies and electron distributions of the HOMO and LUMO of the dyes. It can be clearly seen that the HOMO orbitals of the two dyes predominantly located on the triazatruxene and the neighboring π -conjugated unit, while the LUMOs delocalized over the rhodanine-3-acetic acid and the π -conjugated unit. As a result, this electron distribution will allow significant charge separation within the dye and hence efficient electron injection from the excited dyes into the TiO₂ electrode.

3.3. Photovoltaic performance

The DSSC performace parameters of the two dyes are measured and displayed in Table 2. The photocurrent density-voltage (J-V)curves are plotted in Fig. 4. The DSSC performances of the dyes are evaluated under AM1.5 G irradiation at 100 mW cm⁻² with 0.16 cm² active surface area. **JY04**-sensitized cell gave a power conversion efficiency (PCE) of 2.47% with a short-circuit photocurrent density (J_{sc}) of 5.89 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 580 mV, and a fill factor (FF) of 0.72. At the same conditions, DSSC based on **JY05** showed a better PCE of 3.60% with a relatively higher $J_{sc} = 8.33$ mA cm⁻² and $V_{oc} = 617$ mV. Compared to **JY04**, the significant improvement of photovoltaic performances for **JY05** may be attributed to the more effective electron injection and slower charge recombination rate. For example, the LUMO energy



Fig. 3. Frontier orbitals optimized at the B3LYP/6-31G level.

 Table 2

 Photovoltaic performance of IY04 and IY05 with N719 as reference.^a

Dye	V _{oc} /mV	$J_{\rm sc}/{ m mA~cm^{-2}}$	FF	η/%
JY04	582	5.89	0.72	2.47
JY05	617	8.33	0.70	3.60
N719	734	16.9	0.63	7.82

 $^{\rm a}$ Active area 0.16 cm²; Electrolyte is composed of 0.3 M DMPII, 0.1 M Lil, 0.05 M I₂, and 0.5 M 4-*tert*-butyl pyridine in acetonitrile; Under AM 1.5 G irradiation at 100 mW cm⁻².

levels of the two dyes are in the order of **JY04** (-1.16 V) <**JY05** (-1.02 V), indicating that a DSSC based on **JY05** may exhibit the more effective electron injection from the excited dve into the conduction band of TiO₂. Fig. 5 shows the IPCE spectra of DSSCs based on the two dyes as a function of incident wavelength. Notably, both the two DSSCs exhibited remarkably broad IPCE spectra covering almost the whole visible spectrum with the threshold wavelength up to 800 nm. That is significantly broadened compared to those of their UV-vis absorption spectra in THF solutions, and matches well with the threshold wavelength of the absorption spectra when adsorbed onto TiO₂ films. It suggests that incorporation of rhodanine-3-acetic acid as an electron acceptor in the dyes with good delocalization between the donor and the acceptor can result in a broad IPCE spectrum. As shown in the IPCE curves, the solar cell based on JY04 showed the highest IPCE value of 43.7% at 530 nm. Compared to JY04, the IPCE value of JY05 is much higher, with the highest IPCE value of 67.6% at 500 nm. These results indicated the incorporation of a benzene as the π -conjugated linker is beneficial to obtain the higher power conversion efficiency due to the better light-harvesting ability and a higher photocurrent of JY05. However, the PCEs of JY04 and JY05 were both lower than those cyanoacrylic acid-based triazatruxene dyes which were previously reported by our group [7]. This might be ascribed to the broken electron-transfer path from the dyes to TiO₂ semiconductor caused by the broken (NCH₂COOH) conjugation. Such feature was also supported by the results of Gaussian calculations [17].

3.4. Electrochemical impedance spectroscopy

To elucidate the correlation between the open-circuit photovoltage and the dyes, electrochemical impedance spectroscopy (EIS) was then performed to investigate the effects on charge recombination, transport, and collection [18]. EIS Nyquist plots and



Fig. 4. The photocurrent-voltage (J-V) curves of DSSCs.



Fig. 5. IPCE spectra of the DSSCs based on the two dyes.

Bode phase plots measured in the dark under a forward bias (-0.60 V) with frequency range of 0.1–100 kHz are shown in Fig. 6. The larger semicircle in the lower frequency range in the Nyquist plot represents the interfacial charge transfer resistances (R_{ct}) at the TiO₂/dye/electrolyte interface [19]. A larger radius of the major semicircle means a larger charge transfer resistance. The fitted R_{ct} increases in the order of **JY04** (38.9 Ω) < **JY05** (92.3 Ω) implying



Fig. 6. (a) Nyquist plots and (b) Bode phase plots for DSSCs based on the two dyes measured in the dark under -0.60 V bias.

significantly increasing resistance to charge recombination. This feature coincides with the increase of open-circuit photovoltage, as the suppression of electron recombination between the injected electrons and electrolyte improves open-circuit photovoltage. This trend is in good agreement with $V_{\rm oc}$ values of the two dyes. Electron lifetime (τ) could be calculated from the peak frequency (f) in the lower frequency region in EIS Bode plots using $\tau = 1/(2\pi f)$. Longer electron lifetimes imply increased resistance between the injected electrons and the electrolyte, which consequently improves the V_{oc} . The fitted electron lifetime (τ) increases from **JY04** (20.1 ms) to **JY05** (27.9 ms). The increase in electron lifetime for **JY05** supports more effective suppression of the back reaction of the injected electrons with the iodide/triiodide redox couple in the electrolyte [20], which leads to the improvement of photocurrent and photovoltage and gives substantial enhancement of the device efficiency. This result is also in agreement with the abovementioned observations.

4. Conclusions

In summary, two novel organic dyes based on triazatruxene donor and rhodanine-3-acetic acid acceptor have been successfully synthesized and utilized in dye-sensitized solar cells. Dyes **JY04** and **JY05**, linked by thiophene and benzene conjugations respectively, both showed broad IPCE responses up to 800 nm which covers almost the whole visible light spectrum, suggesting that triazatruxene and rhodanine structures have great potential for constructing photosensitizers. Meanwhile, dye **JY05** exhibited better light-harvesting ability, more efficient electron injection ability, and higher power conversion efficiency than **JY04**. A solar cell based on **JY05** could yield an overall conversion efficiency of 3.60%, with a short-circuit photocurrent density of 8.33 mA cm⁻², an open-circuit photovoltage of 617 mV, and a fill factor of 0.70 under standard conditions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.10.007.

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