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# Influence of different acceptor groups in julolidine-based organic dye-sensitized solar cells

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#### 1. Introduction

#### ABSTRACT

Two novel organic dyes containing julolidine as the electron donor and cyanoacetic acid or rhodanine-3acetic acid as the electron acceptor bridged by bithiophene unit were synthesized. The absorption spectra, electrochemical and photovoltaic properties of the new dyes were extensively investigated. Transient absorption spectra measurements show that both sensitizers are quickly regenerated and the dye cations are efficiently intercepted by the redox mediator. The overall conversion efficiencies of 2.6% and 2.0% were obtained for dye-sensitized solar cells (DSSC) based on the cyanoacetic acid and rhodanine derived dyes, respectively. Compared with the rhodanine terminated dye, the open circuit voltage and the conversion efficiency of solar cell based on the cyanoacetic acid dye are increased about 25% and 30%, respectively. The lower efficiency of solar cell based on rhodanine is mainly resulted from the broken delocalization of the excited state due to the NCH<sub>2</sub>CO<sub>2</sub>H anchor, which affects the electron injection from the rhodanine terminated dye to the conduction band of TiO<sub>2</sub>.

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were synthesized and investigated, such as indoline dyes [6–9], coumarin dyes [10–12], triphenylamine dyes [13–17], cyanine dyes [18,19], carbazole dyes [20–22], phenothiazine dyes [23–26], tetrahydroquinoline dyes [27,28], fluorene dyes [29,30] and perylene dyes [31,32].

Julolidine derivatives have been widely used in electroluminescent devices for good chemical stability, thermal stability and low toxicity [33,34]. Recently, julolidine derivatives have been shown to be promising for DSSCs as photosensitizers due to their strong electron donating effect [35,36]. It's well known that most organic sensitizers are constituted of the electron donor, the electron acceptor and a  $\pi$ -conjugation bridge. Aside from electron donor and  $\pi$ -conjugation bridge, the acceptor segment is widely recognized for its significance for performance control of DSSC. Take the indoline dye for example, D131 with cyanoacetic acid as the acceptor attained the overall conversion efficiency of 5.06% [37]. By replacing cyanoacetic acid to rhodanine-3-acetic acid, the D102 dye exhibited the overall conversion efficiency of 6.1% [6]. We know that the typical acceptor groups are cyanoacetic acid and rhodanine-3-acetic acid. Generally organic dyes with cyanoacetic acid as the anchoring group show better photovoltaic performance

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Dye-sensitized solar cells (DSSCs) have been viewed as prom-

ising candidates for renewable clean energy sources by virtue of

their low manufacturing cost and relatively high efficiency [1]. Dye

sensitizers have been recognized as one of the most important







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Fig. 1. The structures of zinc porphyrin dye, N3, N719, black dye and C106.

[23,38–40]. However, in some cases the organic dye with the rhodanine-3-acetic acid exhibits the higher overall conversion efficiency [41,42].

### 2. Experimental section

#### 2.1. Synthesis

The different acceptors have significant influences on the photovoltaic properties of solar cells based on the dyes. Here we present two novel organic dyes **J5** and **J6** (Scheme 1) containing julolidine as the electron donor and either cyanoacetic acid or rhodanine-3-acetic acid as the electron acceptor bridged by a bithiophene unit. The effects of different acceptor groups (cyanoacetic acid and rhodanine-3-acetic acid) in two novel julolidine-dye photosensitizers (**J5** and **J6**) on the optical properties, electrochemical properties and photovoltaic performance were studied.

The structures of the **J5** and **J6** are shown in Scheme 1. The synthetic pathway of these two dyes is shown in Scheme 2. All solvents and chemicals used in this work were pure grade and were used without further purification. The **J**–**Br** was synthesized by bromination with N-bromosuccimide (NBS) in *N*,*N*-dimethylformamide (DMF). The Suzuki coupling of **J**–**Br** with 1.2 equiv of 2,2'-bithiophene-5-boronic acid pinacol ester yielded **JT**. **JT**–**CHO** was prepared from **JT** *via* the Vilsmeier reaction. The **J5** dye and **J6** dye were produced from the aldehyde **JT–CHO** with



Scheme 1. Molecular structures of D131, D102, J5 and J6.



Scheme 2. Synthetic route to J5 and J6. (a) NBS, DMF, room temperature, 5 h; (b) 2,2'-bithiophene-5-boronic acid pinacol ester, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, 1,4-dioxane, reflux, 24 h; (c) POCl<sub>3</sub>, DMF, reflux, 4 h; (d) cyanoacetic acid or rhodanine-3-acetic acid, CH<sub>3</sub>CN, piperidine, reflux, 15 h.

cyanoacetic acid or rhodanine-3-acetic acid *via* the Knoevenagel reaction.

#### 2.1.1. 9-Bromo-julolidine (J-Br)

A 10 mL DMF solution of julolidine (675 mg, 3.90 mmol) and NBS (832 mg, 4.68 mmol) was stirred for 5 h at room temperature. The crude product was purified by silica column chromatography (hexane/methylene chloride = 3/1) to obtain **J**–**Br** (786 mg, 80%) as a red oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm: 6.87 (s, 2H), 3.10 (t, 4H, J = 5.50 Hz), 2.70 (t, 4H, J = 6.35 Hz), 1.94 (m, 4H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm: 142.0, 129.3, 123.7, 107.3, 50.0, 27.6, 21.9. IR (KBr, cm<sup>-1</sup>): 3045, 2935, 2836, 1581, 1506, 1462, 1446, 1310. TOFMS-EI (m/z): calcd. for (M)<sup>+</sup> C<sub>12</sub>H<sub>14</sub>NBr: 251.0310, found: 251.0309.

#### 2.1.2. 9-(2,2'-Bithiophen-5-yl)-julolidine (JT)

The mixture of **J**–**Br** (582 mg, 2.31 mmol), 2,2'-bithiophene-5boronic acid pinacol ester (810 mg, 2.77 mmol), Tetrakis (triphenylphosphine) palladium (0) (61 mg, 0.05 mmol) and potassium carbonate (2 mL, 10% aq.) in 1,4-dioxane (25 mL) was heated under reflux for 24 h under a argon atmosphere. The crude product was purified by column chromatography (petroleum ether/methylene chloride = 3/1) to obtain **JT** (608 mg, 78%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm: 7.15 (d, 1H, *J* = 5.0 Hz), 7.12 (d, 1H, *J* = 3.0 Hz), 7.06 (d, 1H, *J* = 3.5 Hz), 7.03(s, 2H), 6.99 (d, 1H, *J* = 6.5 Hz), 6.98 (d, 1H, *J* = 3.5 Hz), 3.15 (t, 4H, *J* = 5.5 Hz), 2.77 (t, 4H, *J* = 6.2 Hz), 1.99 (m, 4H, *J* = 6.0 Hz). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ / ppm: 144.2, 142.2, 137.6, 133.4, 127.3, 124.0, 123.1, 122.3, 121.1, 121.0, 120.4, 113.6, 49.5, 27.2, 21.5. IR (KBr, cm<sup>-1</sup>): 3103, 3065, 3026, 2922, 2849, 1607, 1577, 1520, 1496, 1455, 1310. TOFMS-EI (*m*/*z*): calcd. for (M)<sup>+</sup> C<sub>20</sub>H<sub>19</sub>NS<sub>2</sub>: 337.0959, found: 337.0953.

#### 2.1.3. 9-(5'-Formyl-2,2'-bithiophen-5-yl)-julolidine (JT-CHO)

To a solution of IT (450 mg, 1.33 mmol) in DMF (20 mL) was added phosphorus oxychloride (0.15 mL, 1.61 mmol) at 0 °C. The solution was warmed to room temperature and stirred for an additional 2 h. After removal of DMF in vacuo, the reaction mixture was neutralized with sodium acetate and extracted with methylene chloride. The crude product was purified by column chromatography (petroleum ether/acetic ester = 3/1) to obtain **JT**-**CHO** (400 mg, 82%) as a red solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm: 9.82 (s, 1H), 7.63 (d, 1H, J = 4.2 Hz), 7.26 (d, 1H, J = 3.6 Hz), 7.17 (d, 1H, J = 4.2 Hz), 7.04(s, 2H), 7.03 (d, 1H, J = 4.2 Hz), 3.19 (t, 4H, J = 5.7 Hz), 2.77 (t, 4H, J = 6.3 Hz), 1.98 (m, 4H, J = 6.0 Hz). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm: 182.5, 148.3, 143.4, 140.7, 137.9, 132.3, 127.5, 124.7, 123.2, 121.7, 121.4, 120.7, 50.1, 27.9, 22.0. IR (KBr, cm<sup>-1</sup>): 3081, 3057, 3037, 2930, 2850, 2791, 2741, 1661, 1606, 1578, 1519, 1500, 1469, 1452, 1312. FTMS-ESI (*m*/*z*): calcd. for (M)<sup>+</sup> C<sub>21</sub>H<sub>19</sub>NOS<sub>2</sub>: 365.0897, found: 365.0903.

# 2.1.4. 2-Cyano-3-(5'-julolidinyl-2,2'-bithiophen-5-yl)acrylic acid (**J5**)

An acetonitrile solution (25 mL) of **JT–CHO** (142 mg, 0.39 mmol), cyanoacetic acid (40 mg, 0.47 mmol) and piperidine (0.2 mL) was heated under reflux for 8 h under a argon atmosphere. After removal of acetonitrile in vacuo, the crude product was purified by column chromatography (methylene chloride/ methanol = 7/1) to obtain **J5** (135 mg, 80%) as a red solid. <sup>1</sup>H NMR (500 MHz, DMSO- *d*<sub>6</sub>):  $\delta$ /ppm: 8.29 (s, 1H), 7.80 (d, 1H, *J* = 3.5 Hz), 7.44 (d, 1H, *J* = 2.9 Hz), 7.41 (d, 1H, *J* = 4.0 Hz), 7.21 (d, 1H, *J* = 3.5 Hz), 7.02 (s, 2H), 3.11 (t, 4H, *J* = 5.0 Hz), 2.65 (t, 4H, *J* = 5.6 Hz), 1.82 (m, 4H, *J* = 5.5 Hz). <sup>13</sup>C NMR (500 MHz, DMSO- *d*<sub>6</sub>):  $\delta$ /ppm: 163.8, 147.2, 145.2, 144.5, 143.0, 140.5, 133.5, 130.9, 128.0, 124.0, 123.7, 121.7, 121.0, 119.4, 117.6, 100.7, 49.2, 27.1, 21.2. IR (KBr, cm<sup>-1</sup>): 3416, 3072, 3032, 2922, 2849, 2210, 1672, 1606, 1579, 1537, 1489, 1369, 1312. FTMS-ESI (*m*/*z*): calcd. for (M–H)<sup>-</sup> C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 431.0884, found: 431.0883.

#### 2.1.5. 2-(5-(5'-julolidinyl-2,2'-bithiophen-5-yl)-4-oxo-2thioxothiazolidin-3-yl)acetic acid (**16**)

A procedure similar to that for **J5** but with rhodanine-3-acetic acid (74 mg, 0.39 mmol) instead of cyanoacetic acid was used. The crude product was purified by column chromatography (methylene chloride/methanol = 6/1) to obtain **J6** (156 mg, 89%) as a red solid. <sup>1</sup>H NMR (500 MHz, DMSO- *d*<sub>6</sub>):  $\delta$ /ppm: 8.08 (s, 1H), 7.73 (d, 1H, *J* = 4.0 Hz), 7.48 (d, 1H, *J* = 4.0 Hz), 7.44 (d, 1H, *J* = 3.5 Hz), 7.23 (d, 1H, *J* = 3.5 Hz), 7.04 (s, 2H), 3.14(t, 4H, *J* = 5.5 Hz), 2.68 (t, 4H, *J* = 6.0 Hz), 1.85 (m, 4H, *J* = 5.5 Hz). <sup>13</sup>C NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ /ppm: 191.6, 166.0, 164.1, 151.2, 147.5, 146.0, 138.1, 133.2, 131.2, 129.6, 128.3, 127.9, 123.9, 122.7, 121.3, 119.0, 118.5, 49.3, 44.8, 27.0, 21.3. IR (KBr, cm<sup>-1</sup>): 3448, 3063, 3025, 2920, 2848, 1730, 1693, 1604, 1573, 1522, 1494, 1463, 1365, 1314, 1117. FTMS-ESI (*m*/*z*): calcd. for (M + H)<sup>+</sup> C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S<sub>4</sub>: 539.0586, found: 539.0577.

#### 2.2. Preparation of dye-sensitized TiO<sub>2</sub> thin films

The colloidal TiO<sub>2</sub> nanoparticle fabrication process was carried out according to the previous paper [43]. Firstly, the TiO<sub>2</sub> paste was screen-printed onto FTO coated glass (TEC–15, LOF), then sintered at 450 °C for 30 min under air. The TiO<sub>2</sub> thin-film electrode of 10  $\mu$ m thickness was obtained, which was measured by a profilometer (XP–2, AMBIOS Technology Inc., USA). After the film preparation, the films were calcined at 450 °C for 30 min in air. Afterward, the TiO<sub>2</sub> films were immersed in 0.3 mmol L<sup>-1</sup> ethanol solution of the dyes for 12 h.

The solar cell used for photovoltaic measurements consisted of a dye-adsorbed  $TiO_2$  electrode, a counter electrode, a 60  $\mu$ m thermal adhesive film (Surlyn, DuPont) and an organic electrolyte. The

platinized counter electrodes were fabricated by spraying H<sub>2</sub>PtCl<sub>6</sub> solution on FTO, followed by heating at 410 °C for 20 min [44]. The organic electrolyte solution was filled from a hole made on the counter electrode. The active area of the dye-coated TiO<sub>2</sub> film electrode was 0.5 cm  $\times$  0.5 cm = 0.25 cm<sup>2</sup>.

#### 2.3. Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker Avance 500 spectrophotometer with the chemical shifts against tetramethylsilane (TMS). FTIR spectra were acquired on a NICOLET 8700 infrared spectrophotometer. Mass spectra (MS) were obtained using a GCT-TOF and LTQ Orbitrap XL Mass Spectrometer. The absorption spectra of the two dyes and the absorption of the two dye sensitized TiO<sub>2</sub> films were recorded by a UV–Vis spectrophotometer (U–3900H, Hitachi, Japan). Cyclic voltammograms (CV) were carried out on a CHI-660d electrochemical analyzer in a three-electrode electrochemical cell with a Pt disk working electrode, an SCE reference electrode and a platinum wire counter electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 mol  $L^{-1}$  tetrabutylammonium perchlorate (TBAP) in DMF at a scan rate of 100 mV s<sup>-1</sup> using ferrocene ( $E_{Fc/Fc}^{0+} = +0.63$  V vs NHE) as inner standard at the end of each measurement. Transient absorption spectra measurements were performed on an LP920 laser flash spectrophotometer in conjunction with a nanosecond tunable OPOLette 355II laser. The current-voltage (I-V) characteristics of the DSSC were measured under AM 1.5 (100 mW cm<sup>-2</sup>) illumination which was provided by a 3A grade solar simulator (Newport, USA, 94043A, calibrated with a standard crystalline silicon solar cell). The incident photon to current conversion efficiency (IPCE) was performed on QE/IPCE measurement kit (Newport, USA).

#### 2.4. Computations

To gain further insight into the molecular structure and electron distribution of **J5** and **J6** dyes, density functional theory (DFT) calculations using the Gaussian 09 program package [45] were performed at a B3LYP/ $6-31G^*$  level for the geometry optimization. The excitation transitions of the two dyes were calculated using time-dependent density functional theory (TD–DFT) calculations at the same level.

#### 3. Results and discussion

#### 3.1. UV–Vis absorption spectra

The UV–visible absorption spectra of **J5** and **J6** in ethanol are compared in Fig. 2. These two dyes exhibit two mainly distinct absorption bands. The UV absorption is ascribed to a localized aromatic  $\pi - \pi^*$  transition and the visible absorption is of an intramolecular charge transfer (ICT) between the julolidine donor and terminal acceptor. The maximum absorption peaks in visible spectrum and the corresponding  $\varepsilon$  values of **J5** and **J6** are 457 nm  $(1.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$  and 501 nm  $(2.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$ , respectively. **J6** with the rhodanine-3-acetic acid group shows a red-shift of absorption bands compared with **J5** with the cyanoacetic acid acceptor group. The bathochromic shift which is desirable for harvesting light from the solar spectrum should be assigned to the extension of  $\pi$ -conjugated system through the 4oxo-2-thioxothiazolidine ring (rhodanine ring).

When **J5** and **J6** are adsorbed onto the  $TiO_2$  surface, the absorption spectra of the two dyes are broadened and blue-shifted as compared to those in solution (Fig. 3), indicating strong interactions between the dyes and the semiconductor surface. Such



**Fig. 2.** Absorption spectra of **J5** and **J6**  $(3 \times 10^{-5} \text{ mol } L^{-1})$  in ethanol.

blue shifts of the absorption spectra by adsorption on the TiO<sub>2</sub> film have also been observed in other organic dyes [11,46,47]. It can be seen that the absorption peak of the TiO<sub>2</sub> electrodes sensitized by **J5** and **J6** is blue-shifted by 42 nm and 4 nm as compared to the solution spectra, respectively. The blue-shifted values of the two dyes may be the result of H-type aggregation of the dyes on the TiO<sub>2</sub> surface. On the other hand, **J5** dye has a larger blue-shift as compared to **J6** dye, indicating that **J5** dye has a greater tendency to aggregate on TiO<sub>2</sub>.

#### 3.2. Electrochemical properties

The ground-state oxidation potentials  $E_{(S+/S)}$  of **J5** and **J6** dyes are obtained from cyclic voltammetry, and the results are summarized in Table 1. As is shown in Fig. 4, the oxidation potentials of **J5** and **J6** are more positive than the  $I^-/I_3^-$  redox couple (~0.4 V vs NHE), ensuring that there is enough driving force for dye regeneration efficiently through the recapture of the injected electrons from I<sup>-</sup> by the oxidized dyes. The excited-state oxidation potentials for the **J5** and **J6** are more negative than the conduction-band-edge energy level of the TiO<sub>2</sub> electrode (-0.5 V vs NHE), indicating that the electron injection from the excited dye to TiO<sub>2</sub> should be energetically favorable. Therefore, the two dyes can be used as sensitizers for feasible electron transfer in DSSCs.

#### 3.3. Computational studies

To gain insight into the geometrical, electronic and optical properties of **J5** and **J6**, DFT calculations have been performed using



Fig. 3. Absorption spectra of J5 and J6 adsorbed on  ${\rm TiO}_2$  film.

Table 1		
The absorption, emission and electrochemical properties of J	<b>5</b> and ]	6

Dye	Abs $\lambda^a_{max}/nm$ $(\epsilon^b/L mol^{-1} cm^{-1})$	Em λ <sup>a</sup> <sub>ex</sub> /nm	E <sup>0</sup> <sub>(S+/S)</sub> <sup>c</sup> /V (vs NHE)	E <sub>0-0</sub> <sup>d</sup> /V (Abs/Em)	E <sup>0</sup> <sub>(S+/S*)</sub> <sup>e</sup> /V (vs NHE)
J5	457	508	0.66	2.53	-1.87
J6	$(1.0 \times 10^{\circ})$ 294 $(2.2 \times 10^{4})$	581	0.65	2.26	-1.61
	$(2.3 \times 10^{-}),$ 501 (2.2 × 10 <sup>4</sup> )				

 $^a$  Absorption and emission spectra were measured in ethanol  $(3.0\times 10^{-5}\mbox{ mol }L^{-1}).$ 

 $^{\rm b}\,$  The molar extinction coefficient at  $\lambda_{max}$  of the absorption spectra.

 $^{\rm c}$  The highest occupied molecular orbital (HOMO) energy levels of the dye were measured in DMF with 0.1 mol  $L^{-1}$  TBAP as supporting electrolyte, scanning rate: 100 mV s^{-1}.

 $^{\rm d}$   $E_{0-0}$  transition energy, estimated from the intersection between the absorption and emission spectra in ethanol.

<sup>e</sup> The  $E^{0}_{(S+/S^{*})}$  of the dyes were calculated from  $E^{0}_{(S+/S)}-E_{0-0}$ .

the B3LYP exchange correlation functional. The molecular orbital spatial distributions from HOMO–3 to LUMO+2 for **J5** and **J6** are shown in Fig. 5. It can be found that HOMO, HOMO–1 and HOMO–3 mainly distribute at the julolidine moiety and bithiophene unit while LUMO and LUMO+1 at the bithiophene unit and anchoring carboxylic group for both dyes. The LUMO electron density geometry distribution of **J5** on the acceptor is located on the cyanoacetic acid group, but for **J6** on the acceptor it is mainly concentrated on the rhodanine framework, especially on the carbonyl and thiocarbonyl due to the broken (NCH<sub>2</sub>CO<sub>2</sub>H) conjugation for **J6**. Consequently, it prevents electrons from being effectively injected into the TiO<sub>2</sub> conduction band *via* the carboxyl group for the **J6** dye, which finally leads to lower  $J_{sc}$  and  $\eta$ . This agrees with the lower photon-to-current conversion efficiency of **J6** observed experimentally.

The major electron excitations and corresponding electron transition are listed in Table 2. It can be found that the broad band in the 420–700 nm region for **J6** is composed of two electron excitations calculated at 459 and 668 nm. The band in the 380–650 nm region for **J5** is composed of two electron excitations calculated at 422 and 634 nm. The electron excitations of **J6** are red-shifted compared with those of **J5**, which corresponds well with the experimental result. The broad band in the 360–420 nm region for **J6** is composed of several electron excitations calculated around 340 nm. Similar electron excitations are also observed for **J5** in this region, which also corresponds very well with the experimental result. Although **J5** and **J6** have similar absorption bands in the



Fig. 4. Cyclic voltammograms of J5 and J6 in DMF.



Fig. 5. Molecular orbital distribution of J5 and J6.

360–600 nm region, the nature of the electron excitations are different. The longest wavelength electron excitations of both dyes are composed of electron transfer from HOMO to LUMO. The electron excitations around 420 nm, however, are composed of electron transfer from HOMO–1 to LUMO for **J5** while HOMO–3 to LUMO and HOMO to LUMO+1 for **J6** as shown in Table 2.

#### 3.4. Transient absorption spectra measurements

Transient absorption spectra experiments were performed to clarify the dye cation dynamics of interception by iodide [48,49]. Fig. 6 presents the transient absorption spectra of **J5** stained onto

Table 2			
Major electron excitations	and electron	transitions	of <b>J5</b> and <b>J6</b> .

Molecule	Wavelength (oscillator strength)	Electron transfer
J5	634 nm (f = 0.987)	HOMO $\rightarrow$ LUMO (71%)
	422 nm (f = 0.657)	HOMO-1 $\rightarrow$ LUMO (67%)
	273 nm (f = 0.147)	HOMO-1 $\rightarrow$ LUMO+1 (39%)
	206 nm (f = 0.198)	Homo-2 $\rightarrow$ Lumo+2 (39%)
	204 nm (f = 0.129)	HOMO $-3 \rightarrow$ LUMO $+2$ (35%)
	200 nm (f = 0.110)	Homo-3 $\rightarrow$ Lumo+2 (30%)
J6	668 nm (f = 1.040)	HOMO $\rightarrow$ LUMO (71%)
	459 nm (f = 0.732)	HOMO $-3 \rightarrow$ LUMO (67%)
	412 nm (f = 0.096)	Homo $\rightarrow$ LUMO+1 (67%)
	341 nm (f = 0.072)	Homo $\rightarrow$ Lumo+2 (68%)
	299 nm (f = 0.066)	HOMO-6 $\rightarrow$ LUMO (46%)
	273 nm (f = 0.066)	HOMO-1 $\rightarrow$ LUMO+2 (43%)

TiO<sub>2</sub> with pure acetonitrile and in the presence of redox electrolyte (EL) under similar conditions. The transient optical signal observed at  $\lambda = 580$  nm. In acetonitrile, the decays are well fitted by a single exponential with a lifetime  $\tau_b = 120 \ \mu s$  and 64  $\mu s$  for **J5** and **J6**, respectively. The corresponding rate constants of back-electron transfer are  $8.3 \times 10^3$  s<sup>-1</sup> and  $1.6 \times 10^4$  s<sup>-1</sup>. Obviously, the recombination rate is observed to be significantly enhanced by replacing cyanoacetic acid with rhodanine-3-acetic acid. In the presence of acetonitrile based redox electrolyte, a much faster decay of the dye oxidized state was observed, showing that the reduction of the dye cation by iodide is competing efficiently with charge recombination. The decays are well fitted by a single exponential with a lifetime  $\tau_r = 1.9 \ \mu s$  and 1.8  $\mu s$  for **J5** and **J6**, respectively. The corresponding rate constants are  $5.2 \times 10^5 \text{ s}^{-1}$  and  $5.7 \times 10^5 \text{ s}^{-1}$ . The time constant for the reduction of J5 cation is pretty similar to that of I6. Even if the rate constants of both back-electron transfers are dissimilar in the cases of **J5** and **J6**, the  $\tau_b/\tau_r$  branching ratios of over 35 for the two dyes imply that at least 97% of oxidized dye cations are intercepted by electron donation from iodide, resulting in very efficient dye-regeneration.

#### 3.5. Solar cell performance

The spectra of incident photon-to-current conversion efficiency (*IPCE*) for solar cells based on **J5**, **J6** dyes and **N719** dye as a reference are shown in Fig. 7. The *IPCE* value of **J5**-based DSSC exceeds 60% in



**Fig. 6.** The transient absorption spectroscopy of **J5** stained onto TiO<sub>2</sub>. The kinetics observed with acetonitrile (ACN) and in the presence of redox electrolyte (EL) under similar conditions.



Fig. 7. Incident photon-to-current conversion efficiency spectra for DSSCs based on J5 and J6 dyes.

a spectral range from 380 nm to 530 nm and reaches its maximum of 70% at 460 nm. For **J6**-based cell, the *IPCE* exceeds 40% in a range of 430 nm—570 nm and reaches its maximum of 42% at 460 nm. It can be seen that **J5** gives higher *IPCE* value between 300 nm and 580 nm than **J6** dye, however, the higher *IPCE* value of **J6** may be due to the wider absorption spectra above 580 nm. On the other hand, the *IPCE* values for **J5** and **J6** obviously decrease after 850 nm, which can be attributed to the decrease of light harvesting properties.

Fig. 8 shows the *I-V* curves of DSSCs based on **J5** and **J6** dyes, and the corresponding data are summarized in Table 3 in comparison with that of N719 dye. Under standard global AM 1.5 solar irradiation, the J5 sensitized solar cell gives a short circuit photocurrent density ( $J_{sc}$ ) of 10.01 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{oc}$ ) of 410 mV, a fill factor (*FF*) of 0.64, corresponding to an overall conversion efficiency  $\eta$  of 2.6%. Under the same conditions, the **J6** sensitized cell gives a  $J_{sc}$  of 9.48 mA cm<sup>-2</sup>, a  $V_{oc}$  of 329 mV, and a FF of 0.64, corresponding to an overall conversion efficiency of 2.0%. Under similar test conditions, the N719 dye gives a referenced  $\eta$  value of 6.7%. Compared with **J6**, the V<sub>oc</sub> and the conversion efficiency of solar cell based on J5 are increased about 25% and 30%, respectively. The lower efficiency of solar cell based on J6 is mainly due to the broken delocalization of the excited state, which affects the electron injection from J6 to the conduction band of TiO<sub>2</sub>.



**Fig. 8.** Current density (*J*)-voltage curves (*V*) of DSSCs based on **J5** and **J6**. The J-V characteristics of the cells measured under dark conditions are shown in the lower part of this figure.

#### Table 3

Photovoltaic performance of DSSCs based on **15** and **16** dyes <sup>a</sup> comparing with the N719 dye.<sup>a</sup>

Dye	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m mV}$	FF	ŋ/%
J5 <sup>ь</sup> I6 <sup>ь</sup>	10.01 9.48	410 329	0.64 0.64	2.6 2.0
N719 <sup>c</sup>	11.95	756	0.74	6.7

Solar irradiating: AM 1.5 G (100 mW cm<sup>-2</sup>); working area: 0.25 cm<sup>2</sup>. The electrolyte was a solution of 0.6 mol  $L^{-1}$  1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 mol L<sup>-1</sup> Lithium iodide (LiI) and 0.1 mol L<sup>-1</sup> iodine (I<sub>2</sub>) in acetonitrile.

<sup>c</sup> The organic electrolyte solution was a mixture of 0.6 mol  $L^{-1}$  DMPII. 0.1 mol  $L^{-1}$ LiI, 0.1 mol L<sup>-1</sup> I<sub>2</sub> and 0.5 mol L<sup>-1</sup> 4-tert-butylpyridine (TBP) in acetonitrile.

#### 4. Conclusions

In summary, we have synthesized two organic  $D-\pi-A$  dives by employing bithiophene unit as  $\pi$ -conjugated linker in combination with the julolidine donor to evaluate the effect of acceptors on the performance by using the cyanoacetic acid or rhodanine-3acetic acid. Theoretical calculations show that the delocalization of the excited state is broken for J6, which affects the electron injection from J6 to the conduction band of TiO<sub>2</sub>. Transient absorption measurements show that both sensitizers are quickly regenerated and the dye cations are efficiently intercepted by the redox mediator. Besides, the recombination rate is observed to be significantly enhanced by replacing cyanoacetic acid to rhodanine-3-acetic acid. Compared with J6, the Voc and the conversion efficiency of solar cell based on J5 are increased by about 25% and 30%, respectively. The results indicate that cyanoacetic acid acceptor gives a DSSC with better properties than that of rhodanine-3-acetic acid acceptor in the julolidine dyes with a bithiophene  $\pi$ -conjugated linker. It was expected that higher efficiency could be achieved by adjusting the molecular structure of julolidine dyes.

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