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# **RSC** Advances



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Five new organic D-A- $\pi$ -A sensitizers containing benzothiadiazole or benzotriazole as auxiliary electron withdrawing units were synthesized and successfully applied in dye-sensitized solar cells. It was found that the DSSCs based on these dyes could achieve high open-circuit voltage performance and high overall conversion efficiency.

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#### Rigid triarylamine-based D-A- $\pi$ -A Structural Organic Sensitizers for Solar Cells: Significant Enhancement of Open-Circuit Photovoltage with Long Alkyl Group

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Five new organic D-A- $\pi$ -A sensitizers **DIA6-DIA10** containing benzothiadiazole (**BTD**) or benzotriazole (**BTZ**) as auxiliary electron withdrawing units have been synthesized. Their photophysical, electrochemical and photovoltaic properties have been studied. Consequently, although all of these dyes have long alkyl chains grafted on  $\pi$ -bridge, DSSCs with dyes containing **BTZ** unit displayed higher open circuit voltages (757–829 mV) than those containing **BTD** unit (682–712 mV). This may be because that the nitrogen-based heterocyclic group of **BTZ** can lift the conduction band edge and reduce charge recombination arise from the absence of sulfur atom. Benefited from it and the introduction of alkyl chains on the nitrogen atom, DSSCs with one dye containing **BTZ** and thieno[3,2-*b*]thiophene (**TT**) as the  $\pi$ -spacer (**DIA7**) showed the highest open circuit voltage ( $V_{oc} = 829$  mV). The addition of one more thiophene unit to **DIA6** broadens the absorption spectra, leading **DIA8** device to produce the largest photocurrent. Among these sensitizers, the best photovoltaic performance was obtained by **DIA8** device: a short circuit photocurrent density ( $J_{sc}$ ) of 13.45 mA cm<sup>-2</sup>, an open-circuit photovoltage ( $V_{oc}$ ) of 757 mV, and a fill factor (*FF*) of 70%, corresponding to an overall conversion efficiency ( $\eta$ ) of 7.15% which <sup>20</sup> reached 93% of the reference dye **N719**-based cell under standard global AM 1.5 solar light conditions.

#### Introduction

Dye-sensitized solar cells (DSSCs) have been considered as a promising, sustainable and environmental friendly energy device to meet the demands of mankind in the future.<sup>1-2</sup> Up to now, a <sup>25</sup> high photo-to-electricity conversion yield ( $\eta$ ) exceeding 12.0% under standard AM 1.5 sunlight irradiation has been obtained by DSSCs based on Ru-complex dyes.<sup>3</sup> Compared with metal complexes, the metal-free sensitizers have also attracted considerable scientific attention due to their low cost, facile <sup>30</sup> structural modifications, easier preparation and purification.<sup>4</sup> Generally, donor- $\pi$ -acceptor (D- $\pi$ -A) structure is the most common characters of organic dyes.<sup>5</sup> Recently, Tian and coworkers have put forward a so called "D-A- $\pi$ -A" structure, which introduces an auxiliary acceptor between the donor and  $\pi$ 

<sup>35</sup> bridge to further optimize the HOMO and LUMO levels and broaden the absorption spectra.<sup>6</sup>

As is well-known, short circuit photocurrent density  $(J_{sc})$  and open circuit voltage  $(V_{oc})$  have become the primary concern in the design of dyes, because they directly influence the overall 40 conversion efficiency. Dyes with high molar extinction coefficients ( $\varepsilon$ ) and broad absorption spectra are advantageous to the light harvesting of DSSCs, thus beneficial to get high  $J_{sc}$ values.<sup>7</sup> Besides, high  $V_{oc}$  values can be obtained by preventing the intermolecular  $\pi$ - $\pi$  stacking among sensitizers and keeping I<sub>3</sub><sup>--</sup>

<sup>45</sup> ions away from the TiO<sub>2</sub> electrode surface in the DSSCs.<sup>8</sup> Recently a series of sensitizers bearing semi-rigid<sup>9</sup> or rigid<sup>10</sup> planar<sup>11</sup> triphenylamine donors were reported, the efficiency are much better than simple triarylamine based dyes. In our previous study, we have synthetized a rigid amine electron donor with a <sup>50</sup> two-locking structure which was proved to be helpful to increase the  $\varepsilon$  of the corresponding dyes as well as the lifetime of electrons injected into TiO<sub>2</sub> conduction band.<sup>12</sup> The  $J_{sc}$  of these dyes based DSSCs can indeed display a good performance as a result of good light-harvesting ability. However, the relatively low  $V_{oc}$  became a <sup>55</sup> drawback, due to dye aggregation and high rate of charge recombination. Herein, we re-examine our concept by introducing long alkyl chains on the  $\pi$ -spacer. Based



Scheme 1 Molecular structures of dyes (DIA6-DIA10)

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Scheme 2 Synthetic route to dyes DIA6-DIA10.

- <sup>5</sup> on that, we have designed and synthesized five new dyes **DIA6**-**DIA10** (Scheme 1) with the D–A– $\pi$ –A configuration using benzothiadiazole (**BTD**) or benzotriazole (**BTZ**) as auxiliary electron withdrawing units. All of these dyes were designed based on the following considerations: 1) the attached alkyl <sup>10</sup> chains could keep sufficient solubility in common organic solvents. More importantly, the introduced alkyl chains can effectively inhibit the intermolecular aggregation functioned as DCA coadsorbents and charge recombination for the purpose of reducing voltage losses;<sup>13</sup> 2) like pyrimidine, and benzimidazole <sup>15</sup> which have been tested as additives in the electrolyte for the sake of increasing  $V_{oc}$ , the nitrogen-containing heterocyclic group of **BTZ** can be expected to improve  $V_{oc}$ .<sup>14</sup> Compared with **BTZ**, **BTD** is a stronger electron-withdrawing unit which can improve the distribution of donor electrons and broaden absorption spectra
- <sup>20</sup> into the NIR region.<sup>15</sup> Here we employ **BTD** and alkyl grafted thiophene as  $\pi$ -spacer, which can be expected to obtain desirable photo response ability and suppressed dark current from TiO<sub>2</sub> to the electrolyte. As **BTZ** unit has some properties different from the **BTD** unit while replacing sulfur atom by nitrogen one, such
- <sup>25</sup> as more electron-rich, thus the effects posed by the two units on the DSSCs performances could be compared with; 3) it's worth mentioning that besides general thiophene or n-hexyl-thiophene units, thieno[3,2-*b*]thiophene (**TT**) unit was also incorporated in the dyes due to its better  $\pi$ -conjugation and smaller geometric
- <sup>30</sup> relaxation energy upon oxidation;<sup>16</sup> 4) different numbers of thiophene or n-hexyl-thiophene units will influence DSSCs performances. Above all, these dyes based DSSCs are expected to have broad response spectra and suppressed charge recombination, thus leading to high performance. In order to

<sup>35</sup> further investigate the DSSCs performance, the stability of dyes and devices was also measured.

#### **Results and Discussion**

#### Synthesis and Characterization

- The synthetic route to the five new dyes **DIA6-DIA10** is depicted <sup>40</sup> in Scheme 2. The starting materials **1** was synthesized according to our previous work.<sup>12</sup> The intermediates **2**, **3**, **B1**, **B2** and **D1-D4** were constructed by common Suzuki coupling, formylation and bromination reaction (detailed synthesis procedures were described in ESI). Among them, the synthesis of **B1** involved the <sup>45</sup> protection and deprotection of formyl group. The key π-spacer
- <sup>45</sup> protection and deprotection of formy group. The key *n*-space moieties **B3**, **B4** were synthesized according to previous report.<sup>17a</sup> The first final product **DIA6** were obtained by the direct condensation of **3** with cyanoacetic acid in the presence of a catalytic amount of piperidine in THF. The other final products
- <sup>50</sup> DIA7-DIA10 were obtained firstly through Suzuki coupling reaction between bromo-substituted materials 1 and corresponding aldehyde precursor, followed by treatment with cyanoacetic acid in the presence of piperidine in THF. The purification of intermediates was performed by flash column <sup>55</sup> chromatography and subsequent HPLC. All the intermediates and target dyes were characterized by standard spectroscopic methods including <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS.

#### **Optical and electrochemical properties**

The UV–Vis absorption spectra of **DIA6-DIA10** in THF and on  ${}_{60}$  TiO<sub>2</sub> films are shown in Fig. 1 and the corresponding data are summarized in Table 1. All of these compounds exhibit one

major broad absorption band in the visible light region which is attributed to the intramolecular charge transfer (**ICT**) between the donor and the acceptor. The absorption maxima in **ICT** band for **DIA6-DIA10** were located at 431, 444, 465, 478 and 510 nm, <sup>5</sup> respectively. The corresponding molar extinction coefficients are  $3.8 \times 10^4$ ,  $5.6 \times 10^4$ ,  $4.6 \times 10^4$ ,  $2.9 \times 10^4$  and  $3.1 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>. The order of these values **DIA7** > **DIA8** > **DIA6** > **DIA10** > **DIA9** are perfectly consistent with that of the corresponding oscillator



**Fig. 1** (a) UV-Vis absorption spectra of **DIA6-DIA10** in THF  $(1 \times 10^{-5} \text{ M})$ ; (b) absorption spectra of **DIA6-DIA10** adsorbed on TiO<sub>2</sub> film.

strengths (*f*) as determined by TDDFT (2.09, 2.07, 1.84, 1.35 and 1.28, respectively). By comparison, it is found that the absorption <sup>15</sup> maximum of **ICT** for **DIA7** is more red-shifted than that of **DIA6**, in that **TT** could enhance the electron delocalization to more extent than thiophene. Owing to the expansion of the conjugation systems, the bathochromic shift by 34 or 32 nm

Table 1 Optical and electrochemical of DIA6-DIA10

(DIA8 or DIA10) is observed when introducing one more <sup>20</sup> thiophene unit into DIA6 or DIA9. To be mentioned, DIA9 with BTD unit exhibits the maximum absorption peak at 478 nm that is red shifted by 47 nm as compared with DIA6 containing BTZ unit which has the same length of chain. The red-shift may arise from the stronger electron-withdrawing ability of BTD unit, thus <sup>25</sup> resulting in stronger ICT effect on the dye molecule.<sup>16d</sup>

When adsorbed on TiO<sub>2</sub>, the dyes have mild changes (5-13nm) with respect to that in solution. Two points could account for this phenomenon: 1) the alkyl chain plays an important role, reducing intermolecular aggregation when sensitizers are absorbed onto <sup>30</sup> the TiO<sub>2</sub> surface; 2) the incorporation of **BTZ** and **BTD** units is beneficial to countervail the deprotonation effect, which contributes to the observed small shift. <sup>17</sup>

The electrochemical behaviors of the dyes were measured by cyclic voltammetry (CV), and the results are given in the ESI. As 35 shown in Table 1, the first oxidation potentials, taken as the HOMO levels of **DIA6-DIA10**, are calculated to be 1.19, 1.25, 1.14, 1.15 and 1.10 V (vs. NHE, same below), respectively, which are more positive than  $I_3/\Gamma$  redox couples (0.4 V), indicating that the oxidized dyes formed after electron injection 40 into the conduction band of TiO<sub>2</sub> could thermodynamically accept electrons from I<sup>-</sup> ions. In particular, the lowest HOMO potential-energy level was found in **DIA7**, which implies that the device made with it may show the most efficient charge regeneration.<sup>18</sup> The LUMO levels of the sensitizers were 45 estimated by the values of  $E_{ox}$  and the 0–0 band gaps ( $E_{0-0}$ ), whilst the latter values were calculated by the onset of absorption spectra in Fig. 1(b). Consequently, all the LUMO values of these dyes (-1.09, -0.98, -0.96, -0.93 and -0.83V, respectively) are more negative than the conduction band  $(E_{cb})$  of TiO<sub>2</sub> (-0.5 V), 50 indicating the electron injection from the LUMO orbital of these sensitizers to the conduction band of TiO<sub>2</sub> were energetically permitted.

#### **Computational analysis**

To gain a better understanding of the geometrical configuration <sup>55</sup> and electronic distribution of the frontier as well as other closelying orbitals, density functional theory (DFT) calculations were carried out. In the calculations, the long alkyl chains in these compounds were replaced by ethyl groups to save computational time while preserving their steric effect. The hybrid B3LYP <sup>60</sup> functional and the Ahlrichs split valence SVP basis set was RSC Advances Accepted Manuscript

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Dye	$f^{a}$	$\lambda_{\rm max}^{\ \ b}/{\rm nm}(\ \epsilon/10^4 {\rm M}^{-1} {\rm cm}^{-1})$	$\lambda_{max}^{c}/nm$ on TiO <sub>2</sub>	Adsorbed amount <sup>d</sup> (mol cm <sup>-2</sup> )	$E_{\theta \cdot \theta}{}^e$	$E_{HOMO}^{f}(\mathbf{V})$	$E_{LUMO}^{g}(\mathbf{V})$
DIA6	1.84	431 (3.8)	426	$8.6 \times 10^{-8}$	2.28	1.19	-1.09
DIA7	2.09	444 (5.6)	432	$7.6 \times 10^{-8}$	2.23	1.25	-0.98
DIA8	2.07	465 (4.6)	452	$7.5 \times 10^{-8}$	2.10	1.14	-0.96
DIA9	1.28	478 (2.9)	484	$5.5 \times 10^{-8}$	2.08	1.15	-0.93
DIA10	1.35	510 (3.1)	512	$4.8 \times 10^{-8}$	1.93	1.10	-0.83

<sup>*a*</sup> Oscillator strengths at **ICT** bands calculated by DFT/B3LYP; <sup>*b*</sup> Recorded in THF; <sup>*c*</sup> Absorption maximum on TiO<sub>2</sub> transparent films; <sup>*d*</sup> Dye absorbed amounts on 8  $\mu$ m TiO<sub>2</sub> films when THF was used as the solvent for dye loading; <sup>*e*</sup> E<sub>0.0</sub> was estimated from the intersection of absorption and emission spectra; <sup>*f*</sup> HOMOs were internally calibrated with ferrocene (0.59 V versua NHE) measured in CH<sub>3</sub>CN containing 0.1 M (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> with a scan rate of <sup>65</sup> 100 mV s<sup>-1</sup> (working electrode: Pt; reference electrode: SCE); Counter electrode: Pt wire; <sup>*g*</sup> The LUMO was calculated with the expression of *E*<sub>LUMO</sub> =

 $E_{HOMO} - E_{0.0}$ .

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Fig. 2 Dihedral angles between the neighbouring units.

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employed to optimize molecular geometries of the dyes and to s compute their frontier molecular orbitals, using the ORCA program package.<sup>19-21</sup> Subsequent time-denpendent DFT (TDDFT) calculations were performed to gain information of the basis set implemented in Gaussian 09 program package.<sup>22</sup>

As is depicted in Fig. 2, in the ground state, the geometry of <sup>10</sup> the dyes is not planar. For **DIA6-DIA8**, only one major twist was observed in the molecular structure, which is located between the donor and neighbouring  $\pi$ -spacer and the corresponding dihedral angles are 25.4°, 26.0° and 16.4°, respectively. However, for **DIA9** and **DIA10**, the molecules are mainly twisted at two <sup>15</sup> positions: One is located between the donor and neighbouring  $\pi$ spacer and the corresponding dihedral angles are 32.0° and 51.0°; the other is located between the acceptor and the neighbouring  $\pi$ spacer and the corresponding dihedral angles are 31.2° and 31.8°. It is obvious that the structures of **DIA9** and **DIA10** are more <sup>20</sup> twisted than the other dyes. The reason can be explained by that

- the presence of alkyl chain on the thienyl unit may cause steric hindrance, resulting in larger dihedral angles and twisted conformation. This can be further used to explain that the loading amounts of **DIA9** ( $5.5 \times 10^{-8}$  mol cm<sup>-2</sup>) and **DIA10** ( $4.8 \times 10^{-8}$
- $_{25}$  mol cm<sup>-2</sup>) on the TiO<sub>2</sub> surface were lower than that of **DIA6**-**DAI7** (8.6 × 10<sup>-8</sup>, 7.6 × 10<sup>-8</sup> and 7.5 × 10<sup>-8</sup> mol cm<sup>-2</sup>, respectively). Because a more twisted conformation could make the molecule occupy a larger surface area than a molecule of linear shape. <sup>23</sup>

#### 30 DSSCs performance

To investigate the light harvesting ability of **DIA6-DIA10**, DSSCs based on dye-sensitized TiO<sub>2</sub> (12  $\mu$ m) films and the electrolyte in the experimental section were fabricated and the performances were measured. Fig. 3(a) shows the action spectra

<sup>35</sup> of the incident photon-to-current conversion efficiency (IPCE) for DSSCs with these dyes when THF was used as the solvent for dye loading. The IPCE onsets for **DIA6-DIA10** are 620, 630, 680,

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# 650, and 740 nm, respectively, which are broadened significantly with respect to the absorption spectra on sensitized films. This <sup>40</sup> phenomenon could be ascribed to the scattering effect of the large particles in the film and the reflective effect of the Pt counter electrode. The IPCE values of these dyes reached a maximum of 85.1% at 440 nm, 88.2% at 490 nm, 86.2% at 500 nm, 72.6% at 490 nm and 63.2% at 520 nm respectively. The highest IPCE value was achieved by **DIA7** device, which may be a result of the high molar extinction coefficients. Although the IPCE value for **DIA8** device was almost the same as that for **DIA6** and **DIA7** devices, **DIA8** exhibited better performance with broader



**Fig. 3** The performances of DSSCs sensitized by **DIA6-DIA10**: (a) IPCE spectra for DSSCs based on **DIA6-DIA10** with dye baths in THF; (b) *J-V* curves for DSSCs based on **DIA6-DIA10** with dye baths in THF upon AM 1.5 solar light irradiation and under dark condition.

spectra region, indicating that **DIA8** sensitized TiO<sub>2</sub> electrode would generate a higher conversion yield compared to these dyes. The maximum IPCE for **DIA9** and **DIA10** devices were lower than that of the others, which may be attributed to the combined <sup>60</sup> impacts of the electron injection yield from the excited dye to the CB of the TiO<sub>2</sub> (related with the LUMO energy level), the absorption capacity and the amount of dye adsorbed on the TiO<sub>2</sub> film.<sup>24</sup>

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The current density-voltage (J-V) curves of the DSSCs based on these dyes under standard global AM 1.5 solar light conditions (100 mW cm<sup>-2</sup>) are displayed in Fig. 3(b). The detailed parameters, i.e., short-circuit photocurrent  $(J_{sc})$ , open-circuit <sup>5</sup> photovoltage  $(V_{oc})$ , fill factor (FF), and power conversion efficiency  $(\eta)$  are summarized in Table 2. When THF was used as the solvent for dye loading, the DSSCs based on DIA6-DIA10 exhibited inferior conversion efficiency of 5.65%, 6.23%, 7.15%, 5.20% and 5.82%. The  $J_{sc}$  of DSSCs with dyes based on **BTZ** 10 unit decreased in the order of DIA8 > DIA7 > DIA6, which is consistent with that of their corresponding IPCE performance mentioned above. Compared with **DIA9**, the  $J_{sc}$  of **DIA10** device is much higher, despite lower maximum IPCE values, indicating the broader absorption spectra is beneficial to obtain better light-15 harvesting ability and higher light-to-electricity conversion efficiency.

Table 2 The performances of DSSCs based on DIA6-DIA10 in THF.

J₅c/mA cm <sup>-2</sup>	V <sub>oc</sub> /mV	FF (%)	η (%)
9.54±0.26	808±16	73±1	5.65±0.18
10.56±0.28	829±10	<b>71±</b> 1	6.23±0.20
13.45±0.36	757±21	70±2	7.15±0.23
9.71±0.33	<b>712</b> ±14	75±1	5.20±0.33
11.82±0.47	682±12	<b>72±</b> 1	5.82±0.19
17.79±0.29	<b>718±</b> 10	60±2	7.64±0.27
	J <sub>sc</sub> /mA cm <sup>-2</sup> 9.54±0.26 10.56±0.28 13.45±0.36 9.71±0.33 11.82±0.47 17.79±0.29	$J_{sc}/mA \text{ cm}^{-2}$ $V_{oc}/mV$ 9.54±0.26         808±16           10.56±0.28         829±10           13.45±0.36         757±21           9.71±0.33         712±14           11.82±0.47         682±12           17.79±0.29         718±10	$J_{sc}/mA \text{ cm}^2$ $V_{oc}/mV$ FF (%)           9.54±0.26         808±16         73±1           10.56±0.28         829±10         71±1           13.45±0.36         757±21         70±2           9.71±0.33         712±14         75±1           11.82±0.47         682±12         72±1           17.79±0.29         718±10         60±2

<sup>a</sup> The electrolytes was composed of 0.1 M lithium iodide, 0.6 M 1,2dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M I<sub>2</sub>, 0.5 M 4-20 tertbutylpyridine (4-TBP) in acetonitrile (AN) as a liquid electrolyte; <sup>*b*</sup> The electrolytes was composed of 0.1 M DMPII, 0.05 M lithium iodide, 0.03 M I2, 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M guanidinium thiocyanate, and 0.5 M 4-TBP in AN : valeronitrile (85:15, v/v) as a liquid electrolyte. Average of four samples.

The generation of  $V_{oc}$  is related to the charge recombination rate and electron injection efficiency in DSSCs. Among all of the dyes, DIA6-DIA8 based DSSCs (with the BTZ group) showed higher  $V_{oc}$  than **DIA9** and **DIA10** based ones (with **BTD**). There 30 are two possible reasons: 1) compared with **BTD**-based sensitizers, the BTZ unit contains no sulfur element which is attractive to iodine in the electrolyte. Therefore, the BTZ-based sensitizers can decrease the iodine concentration at the vicinity of TiO<sub>2</sub> and reduce charge recombination;<sup>25</sup> 2) the nitrogen-based 35 heterocyclic group of BTZ may lift the conduction band edge of

- TiO<sub>2</sub> and improve  $V_{oc}$ .<sup>6c</sup> Obviously, **DIA7** based DSSCs exhibits the highest open-circuit voltage (829 mV). Two reasons could take account for this phenomenon: 1) since the DIA7 darkcurrent onset potential shifted to a larger value than that of other
- 40 dyes (as shown in Fig. 3(b)), suggesting that DIA7 can inhibit charge recombination between injected electrons and  $I_3^-$  ions in the electrolyte more effectively; 2) DIA7 owned lowest HOMO potential-energy level which leads to sufficient driving force for dye regeneration. It is noteworthy, DIA7 based DSSCs exhibited
- <sup>45</sup> higher values of  $J_{sc}$ ,  $V_{oc}$  and  $\eta$  than **DIA6**, suggesting that as an alternative to thiophene, the TT moiety can be advantageously incorporated into the dye sensitizer as a  $\pi$ -spacer and improve the cell efficiency. On the other hand, introducing an extra  $\pi$ -spacer between the donor and auxiliary acceptor seems to increase the
- $_{50}$  J<sub>sc</sub> of DSSCs due to expanded light response region (for example, **DIA6** and **DIA8**). Such a regular phenomenon may be helpful to design new D-A- $\pi$ -A dyes. The best performance is found in

**DIA8** device, which shows a maximum  $J_{sc}$  of 13.45 mA cm<sup>-2</sup>, a  $V_{qc}$  of 757 mV, a FF of 70% and an  $\eta$  of 7.15%. The high  $\eta$  was 55 mainly attributed to the large  $J_{sc}$  which may be derived from good IPCE performance. Besides, the replacement of sulfur element by nitrogen element may cause the  $V_{oc}$  of **DIA8** device higher than that of DIA9 and DIA10 devices.

#### Electrochemical impedance spectroscopy

60 Electrochemical impedance spectroscopy (EIS) was performed to further elucidate the photovoltaic properties of these dyes. The Nyquist plot and Bode plot are shown in Fig. 4 (a) and 4 (b), respectively. The Nyquist plots for DIA6-DIA10 sensitized cells were measured under a forward bias of -0.70V in the dark with a



Fig. 4 Impedance spectra of DSSCs based on DIA6-DIA10 with dye baths in THF measure at bias -0.70 V in the dark: (a) Nyquist plots; (b) 70 bode phase plots; (c) equivalent circuit of DSSCs based on DIA6-DIA10. The lines of (a) and (b) show theoretical fits using the equivalent circuits (c).

frequency range of 0.1 Hz to 100 kHz. Since the semicircle for Nernst diffusion within the electrolyte was overlapped by the 75 intermediate-frequency large semicircle, only two semicircles were observed in the Nyquist plots. The smaller semicircle at high frequency was assigned to the redox charge-transfer

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response at the Pt/electrolyte interface, while the larger one at the intermediate frequency represented the charge transfer resistance at the TiO<sub>2</sub>/dye/electrolyte interface ( $R_{rec}$ ). It is related to the charge recombination rate, e.g., a larger  $R_{rec}$  indicates a slower <sup>5</sup> charge recombination and therefore a smaller dark current (shown in Fig. 3(b)). The radius of the biggest semicircle  $R_{rec}$  values decreased in the order of **DIA7** > **DIA6** > **DIA8** > **DIA9** > **DIA10**. The detailed data analyzed by software (ZSimpWin) using an equivalent circuit shown in Fig. 4(c) can further <sup>10</sup> demonstrate the results mentioned above. By fitting the EIS spectra to an electrochemical model<sup>26</sup>, several important parameters such as  $R_S$  (the series resistance),  $R_{rec}$  and  $R_{CE}$  (charge transfer resistance at the Pt/electrolyte interface) can be obtained.

Among these parameters,  $R_S$  and  $R_{CE}$  are associated with the <sup>15</sup> smaller semicircle. As listed in Table 3,  $R_S$  and  $R_{CE}$  of these dyes based DSSCs show almost the same value because of the same electrolyte and electrode the devices used. The  $R_{rec}$  of the **DIA6**-

**Table 3** Parameters obtained by fitting the impedance spectra of the DSSCs with sensitizers **DIA6-DIA10**, using the equivalent circuit.

Dye	$R_{s} (\Omega cm^{-2})$	$R_{rec} (\Omega cm^{-2})$	$R_{CE} (\Omega cm^{-2})$	$\tau_e(ms)$
DIA6	13.9	272.6	5.6	136
DIA7	15.8	543.9	12.7	152
DIA8	13.7	113.6	6.0	113
DIA9	15.0	34.4	7.3	86
DIA10	13.7	28.4	7.0	82

**DIA10** dyes are 272.6, 543.9, 113.6, 34.4 and 28.4  $\Omega$ cm<sup>-2</sup>, respectively. The result appears to be consistent with the increase of  $V_{oc}$  in the DSSCs with dyes. The smaller  $R_{rec}$  value means the electron recombination from the TiO<sub>2</sub> to electron acceptors in the <sup>25</sup> electrolyte occurs more easily, thus resulting in lower  $V_{oc}$ . The electron lifetime measured by the relation  $\tau_e = 1/(2\pi f)$  (*f* is the peak frequency) decreased in the order of **DIA7** (152 ms) > **DIA6** (136 ms) > **DIA8** (113 ms) > **DIA9** (86 ms) > **DIA10** (82 ms), while the peak frequency in Bode plot enhanced in the reverse. <sup>30</sup> All of the data mentioned above could well support the order of the  $V_{oc}$  of DSSCs based on these dyes. It is reasonable that **DIA7** device has a high  $V_{oc}$  value due to the long electron lifetime and slow charge recombination rate.

#### **Stability of Dyes and Devices**

- <sup>35</sup> Photo-stability is one of the most important parameters for cell operation for durable application. According to the research by Katoh and coworkers,<sup>27</sup> we measured the absorption spectra of dye-loaded TiO<sub>2</sub> film before and after 30 min of AM 1.5 simulated solar light irradiation, and observed the variation in the
- <sup>40</sup> absorption curves. The details of **DIA6-DIA10** are showed in Fig. S3. It could be observed that the variations were huge before and after light irradiation without the use of UV cutoff filter. However the situation appeared entirely different when the UV cutoff filter at 400 nm was used, suggesting that these dyes were
- <sup>45</sup> easily degraded by ultraviolent light. As shown in Fig.S3 (b), since no distinct absorption peak shifts were observed, sensitizers **DIA6-DIA10** were basically stable. From the comparison of **DIA6** and **DIA7**, the introduction of **TT** instead of thiophene lead to less decrease in absorbance, implying that **DIA7** had a higher the advector of the comparison of the comparison of the comparison of the start of the comparison of the compa
- <sup>50</sup> photo-stability. On the other hand, extending the chain length of the oligothiophene moiety seems to be beneficial to stabilize the oxidized dyes upon light irradiation, such as **DIA6** and **DIA8**.

To further evaluate the long term stability of **DIA7**, **DIA8**based DSSC, a less volatile ionic liquid electrolyte (containing <sup>55</sup> 0.6 M 1-propyl-3-methylimidazolium iodide, 0.15 M iodine, 0.1 M guanidiniumthiocyanate and 0.5 M NMBI in 3methoxypropionitrile) was employed. Table 4 and Fig. 5 shows

 Table 4 Photovoltaic performance of DSSCs based on DIA7 and DIA8 with solvent-free ionic liquid electrolyte.

Dye	J <sub>sc</sub> /mA cm <sup>-2</sup>	V <sub>oc</sub> /mV	FF (%)	η (%)
DIA7	8.99±0.11	693±10	62±1	3.88±0.12
DIA8	$10.85 \pm 0.08$	674±11	62±1	4.54±0.16
60 <sup>a</sup> Average of	f three samples.			

the variations of photovoltaic parameters during a long-term accelerated aging on **DIA7** and **DIA8** based solar cells, keeping constant performance during 500 h aging test under one sun at 60 <sup>65</sup> °C. Upon a continuous 500 h of light soaking, the efficiencies of the DSSCs based on **DIA7** and **DIA8** showed a maximum change of 5.9% and 3.6%. These results suggested that the two dyes are promising candidates for practical application.



**Fig. 5** Variations of photovoltaic parameters  $(J_{sc}, V_{oc}, FF, \text{ and } \eta)$  with aging time for the DSSC devices based on **DIA7-DIA8** and ionic liquid electrolyte under visible-light soaking.

#### Conclusions

<sup>75</sup> In summary, five rigid triarylamine based D-A- $\pi$ -A structural dyes, with **BTD** or **BTZ** as auxiliary electron withdrawing units,

were successfully synthesized and characterized. The result shows that the  $V_{oc}$  values of **DIA6-DIA8** with a **BTZ** moiety are higher than those of **DIA9** and **DIA10** with a **BTD** group. **TT**containing **DIA7** based DSSCs exhibits the highest  $V_{oc}$  of 829 <sup>5</sup> mV due to its lowest HOMO potential-energy level, the long

- electron lifetime and slow charge recombination rate. The additional thiophene or n-hexyl-thiophene in **DIA8** or **DIA10** leads to a significant redshift in the UV-Vis properties and photocurrent response by extending the conjugated system.
- <sup>10</sup> However, owing to the strong steric hindrance caused by n-hexylthiophene unit, a remarkable molecular twist exists in the spacer of **DIA9** and **DIA10**, which decreases the dye-loading amount as well as IPCE values. Because of the broad absorption spectrum and efficient electron injection into the conduction band of TiO<sub>2</sub>, **DIA9** with the large L are whilt the bast performance everyll
- <sup>15</sup> **DIA8** with the large  $J_{sc}$ , exhibits the best performance overall efficiency of 7.15% among these dyes ( $J_{sc}$  of 13.45 mA cm<sup>-2</sup>, a  $V_{oc}$  of 757 mV, and a *FF* of 70%). Based on the above findings, the insertion of an extra  $\pi$ -spacer between the donor and auxiliary acceptor and avoiding the long alkyl chain tightly close to the <sup>20</sup> acceptor are good designs for the D-A- $\pi$ -A structured dyes.

#### Experimental

#### Materials

Optically transparent FTO conducting glass (fluorine doped SnO<sub>2</sub>, transmission >90% in the visible, sheet resistance  $15\Omega$  per 25 square) was obtained from the Geao Science and Educational Co. Ltd. of China and cleaned by a standard procedure. Titania pastes of Ti-Nanoxide T/SP (13 nm) and Ti-Nanoxide 300 were also purchased from there. Tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>), 4-tert-butylpyridine (TBP), 2.4 30 M BuLi solution in hexane and the reaction catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> were obtained from J&K. Lithium iodide, 1,2-dimethyl-3propylimidazolium iodide (DMPII) were from Fluka and iodine (99.999% purity) was from Alfa Aesar. Acetonitrile with HPLC purity was purchased from SK Chemicals. THF was pre-dried 35 over sodium and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. All other chemicals were used as received without further purification. The starting materials 4,7-dibromo-2-octyl-2H-benzo[d][1,2,3]triazole, 4,7-

dibromobenzo[*c*][1,2,5]thiadiazole and 3-bromo-8,8-diethyl-8*H*-<sup>40</sup> indolo[3,2,1-*de*]acridine were commercially available.

#### Instruments and Characterization

NMR spectra were obtained on a Brucker AM 400 spectrometer and HRMS were performed using a Waters LCT Premier XE spectrometer. Elemental analysis was performed on a German 45 elementar vario EL III instrument. The absorption spectra of sensitizers in solution and adsorbed on TiO<sub>2</sub> films were measured with a Varian Cary 500 spectrophotometer. The cyclic voltammograms of dyes were determined with a Versastat II electrochemical workstation (Princeton applied research) using a 50 normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexaflourophosphate (TBAPF<sub>6</sub>) was used as the supporting

- electrolyte in cyanoacetic acid. The electrochemical impedance <sup>55</sup> spectroscopy (EIS) measurements of all the DSSCs were
- performed using a Zahner IM6e Impedance Analyzer

(ZAHNERElektrik GmbH & CoKG, Kronach, Germany). The spectra were scanned in a frequency range from 0.1 Hz to 100 kHz at room temperature with applied potential set at open 60 circuit. The alternate potential amplitude was set at 10 mV.

The DSSCs were evaluated by recording the *J*–*V* curves with a Keithley 2400 source meter under the illumination of an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to <sup>65</sup> 100 mW cm<sup>-2</sup> using a Newport Oriel PV reference cell system (model 91150V). A mask of 0.25 cm<sup>-2</sup> was used to cover around the cell active area. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. The photocurrent action spectra were measured with an IPCE test <sup>70</sup> system consisting of a model SR830 DSP Lock-In Amplifier and a model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp and power supply, and a 7ISW301 spectrometer. Impedance spectra were recorded using a CHI-660c electrochemical station.

#### 75 Fabrication of DSSCs

The pretreatment of transparent conducting oxide (FCO) glass and fabrication of solar cells were performed according to the published procedures.<sup>28</sup> Excepted that the coated TiO<sub>2</sub> film was consisted of a 8  $\mu$ m thin TiO<sub>2</sub> film and a 4  $\mu$ m scattering layer <sup>80</sup> (Ti-Nanoxide 300). DSSCs were fabricated using **DIA6-DIA10** as sensitizers with an effective working area of 0.25 cm<sup>2</sup>, dye adsorbed TiO<sub>2</sub> films pasted onto FCO glass as the working electrode.

#### Synthesis:

#### 5 (E)-2-cyano-3-(5-(7-(8,8-diethyl-8*H*-indolo[3,2,1de]acridin-3-yl)-2-octyl-2*H*-benzo[*d*][1,2,3]triazol-4yl)thiophen-2-yl)acrylic acid (DIA6)

A mixture of compound **3** (651 mg, 1mmol), 2-cyanoacetic acid (320 mg, 4 mmol) and 3 drops of piperidine in 20 ml THF was <sup>90</sup> refluxed for 4 h under N<sub>2</sub> atmosphere. After cooling to r.t., the solvent was removed by rotary evaporation. The residue was purified by column chromatography using silica gel and firstly using pure dichloromethane as the eluent to exclude the impurities and then using THF and methanol mixture (1 : 1) as <sup>95</sup> the eluent to obtain the pure product as light red solid (503 mg, 73%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 9.05 (s, 1H), 8.52 (d, J = 9 1 Hz 1H) 8.44 (d J = 10.4 Hz 1H) 8.31 (d J = 8.3 Hz 1H)

- = 9.1 Hz, 1H), 8.44 (d, J = 10.4 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.22 (m, 2H), 8.12 (d, J = 7.5 Hz, 1H), 8.00 (m, 2H), 7.88 (s, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.45 (q, J = 7.4
- <sup>100</sup> Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 4.93 (t, J = 6.9 Hz, 2H), 2.12 (m, 6H), 1.37 (m, 4H), 1.21 (m, 6H), 0.78 (t, J = 6.5 Hz, 3H), 0.42 (t, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (126 MHz, THF-d<sub>8</sub>),  $\delta$ : 149.45, 144.89, 142.91, 141.94, 137.83, 137.63, 137.31, 137.24, 136.35, 130.86, 129.99, 129.12, 128.20, 127.91, 127.75, 127.50, 125.86, 125.42, 124.34, 124.11, 123.19, 122.92, 121.65, 121.33, 121.00, 119.42, 119.28, 117.90, 114.53, 113.78, 56.72, 46.29, 38.13, 31.48, 28.82, 28.63, 26.28, 22.35, 14.19, 9.76. HRMS (*m*/*z*): [M + H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>44</sub>N<sub>5</sub>O<sub>2</sub>S, 718.3216; found, 718.3213; elemental analysis calcd (%) for C<sub>45</sub>H<sub>43</sub>N<sub>5</sub>O<sub>2</sub>S : C 75.28, H 6.04, <sup>110</sup> N 9.76; found: C 75.11, H 5.74, N 9.65.

(E)-2-cyano-3-(5-(7-(8,8-diethyl-8H-indolo[3,2,1de]acridin-3-yl)-2-octyl-2H-benzo[d][1,2,3]triazol-4yl)thieno[3,2-b]thiophen-2-yl)acrylic acid (DIA7)

Compound DIA7 was synthesized according to the same procedure as that of **DIA6**, as red solid in 74% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 9.05 (s, 1H), 8.57 (s, 1H), 8.50 (d, J =8.9 Hz, 1H), 8.42 (d, J = 9.5 Hz, 1H), 8.29 (d, J = 9.7 Hz, 2H), 5 8.12 (m, 2H), 7.98 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.44 (m, 2H), 7.26 (t, J = 7.4 Hz, 1H), 4.93 (t, J = 6.8 Hz, 2H), 2.11 (m, 6H), 1.36 (m, 4H), 1.21 (m, 6H), 0.78 (t, J = 6.7 Hz, 3H), 0.41 (t, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (126 MHz, THF-d<sub>8</sub>), δ: 146.08, 145.09, 142.99, 141.92, 139.32, 139.10, 10 137.92, 137.73, 137.39, 130.80, 130.09, 129.22, 128.35, 128.04, 127.64, 125.96, 125.63, 125.53, 124.44, 124.26, 124.10, 123.32, 123.05, 122.40, 121.42, 121.10, 119.90, 118.88, 118.02, 114.66, 113.92, 56.84, 46.39, 38.27, 31.62, 29.78, 28.99, 28.75, 26.42, 22.49, 14.33, 9.91. HRMS (m/z):  $[M + H]^+$  calcd for 15 C<sub>47</sub>H<sub>44</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub>, 774.2936; found, 774.2933; elemental analysis calcd (%) for C47H43N5O2S2 : C 72.93, H 5.60, N 9.05; found: C 72.65, H 5.39, N 8.93.

#### (E)-2-cyano-3-(5-(7-(5-(8,8-diethyl-8*H*-indolo[3,2,1de]acridin-3-yl)thiophen-2-yl)-2-octyl-2*H*-

#### 20 benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)acrylic acid (DIA8)

- <sup>25</sup> benzoja j(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(1,2,5) f(2,2,5) f(2,2,5)
- H]<sup>+</sup> calcd for  $C_{49}H_{46}N_5O_2S_2$ , 800.3093; found, 800.3094; elemental analysis calcd (%) for  $C_{49}H_{45}N_5O_2S_2$  : C 73.56, H 5.67, N 8.75; found: C 73.40, H 5.38, N 8.59.

#### (E)-2-cyano-3-(5-(7-(8,8-diethyl-8H-indolo[3,2,1-40 de]acridin-3-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3hexylthiophen-2-yl)acrylic acid (DIA9)

Compound **DIA9** was synthesized according to the same procedure as that of **DIA6**, as dark red solid in 74% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 8.96 (s, 1H), 8.52 (d, J = 8.8 Hz,

- <sup>45</sup> 1H), 8.36 (d, J = 7.5 Hz, 1H), 8.30 (d, J = 6.9 Hz, 3H), 8.24 (s, 1H), 8.12 (dd, J = 7.3, 3.8 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.45 (m, 2H), 7.28 (t, J = 7.4 Hz, 1H), 2.86 (t, J = 7.1 Hz, 2H), 2.12 (m, 4H), 1.67 (m, 2H), 1.34 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H), 0.42 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz,
- <sup>50</sup> THF-d<sub>8</sub>),  $\delta$ : 164.53, 153.51, 152.58, 152.20, 143.98, 137.78, 137.59, 137.37, 133.60, 131.76, 130.03, 129.67, 129.23, 128.24, 128.05, 127.93, 127.69, 125.68, 125.41, 124.17, 123.79, 123.26, 122.92, 121.91, 121.25, 118.53, 117.99, 114.50, 113.56, 46.27, 38.11, 31.30, 30.93, 28.75, 28.56, 22.38, 14.23, 9.75. HRMS <sup>55</sup> (*m/z*): [M + H]<sup>+</sup> calcd for C<sub>43</sub>H<sub>39</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>, 707.2514; found,
- 707.2511; elemental analysis calcd (%) for  $C_{43}H_{38}N_4O_2S_2$  : C 73.06, H 5.42, N 7.93; found: C 72.89, H 5.32, N 7.76.

(E)-2-cyano-3-(5-(7-(5-(8,8-diethyl-8H-indolo[3,2,1-

de]acridin-3-yl)-4-hexylthiophen-2-

### 60 yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)acrylic acid (DIA10)

Compound **DIA10** was synthesized according to the same procedure as that of **DIA6**, as blackish red solid in 76% yield. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 8.43 (d, *J* = 8.7 Hz, 1H), 8.38 (s,

- $^{65}$  1H), 8.28 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 2H), 8.10 (m, 2H), 7.66 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.45 (m, 1H), 7.41 (t, *J* = 5.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 2.78 (m, 4H), 2.12 (ddd, *J* = 31.5, 13.8, 7.3 Hz, 4H), 1.65 (m, 4H), 1.27 (m, 12H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.75 (t, *J* = 6.9
- <sup>70</sup> Hz, 3H), 0.40 (t, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (126 MHz, THF-d<sub>8</sub>), δ: 164.24, 153.93, 151.80, 151.61, 145.25, 140.84, 139.31, 137.82, 137.55, 136.77, 135.97, 131.24, 130.88, 129.96, 129.27, 128.20, 127.80, 127.68, 127.65, 126.73, 126.49, 125.77, 125.35, 124.73, 124.06, 123.14, 122.97, 122.94, 121.13, 121.01, 117.97,
- <sup>75</sup> 117.57, 114.37, 113.76, 46.27, 38.18, 31.34, 31.27, 30.79, 30.56, 29.07, 28.84, 28.67, 28.59, 22.43, 22.39, 14.22, 14.17, 9.74. HRMS (*m*/*z*):  $[M + H]^+$  calcd for C<sub>53</sub>H<sub>53</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>, 873.3331; found, 873.3334; elemental analysis calcd (%) for C<sub>53</sub>H<sub>52</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub> : C 72.90, H 6.00, N 6.42; found: C 72.76, H 5.99, N 6.27.

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#### Notes and references

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† Electronic Supplementary Information (ESI) available: (1) Frontier molecular orbital contours of **DIA6-DIA10**, obtained from single point calculations at the CAM-B3LYP/SVP level of theory; (2) Cyclic voltammograms of dyes attached on 8 µm TiO<sub>2</sub> films; (3) Absorption

- 95 curves of dyes DIA6-DIA10 upon light irradiation of AM 1.5 solar light (30 min) with and without UV cutoff filter at 400 nm; (4) Synthetic procedure of intermediate 2, 3, B1, B2 and D1-D4; (5) Fig. S4-S8 <sup>1</sup>H and <sup>13</sup>CNMR spectrum of DIA6-DIA10. See DOI: 10.1039/b000000x/
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