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YAL SOCIETY CHEMISTRY

## Journal Name

## ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

## Effects of ethynyl unit and electron acceptors on the performance of triazatruxene based dye-sensitized solar cells

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Metal-free organic dyes **JY43–46** based on triazatruxene donor were synthesized for dye-sensitized solar cells (DSSCs), where the effects of ethynyl unit and electron acceptor/anchor were systematically investigated. Compared to dyes **JY45** and **JY46**, **JY43** and **JY44** containing an additional ethynyl unit in the molecular structure show higher molar absorption coefficient, respectively. The strongly electron-withdrawing cyanoacrylic acid seems helpful for dyes to achieve better light harvesting ability than carboxylic acid group, hence for the enhancement of dyes' photocurrent. Notably, dyes **JY43** and **JY45** incorporating carboxylic acid anchor exhibit more effective suppression of charge recombination and longer lifetime of excited electron, therefore delivering a higher photovoltage. Under standard light irradiation (AM1.5G), the dye **JY43** with an ethynyl unit and carboxylic acid in skeleton gives the highest power conversion efficiency of 7.51% in the iodine electrolyte.

## 1. Introduction

Dye-sensitized solar cells (DSSCs), as a promising photovoltaic technology in solar energy utilization, have received widespread attention due to their low cost, easy fabrication, and high photoelectric performance.<sup>1-9</sup> Through years of continuous efforts, tremendous sensitizers have been designed and applied in DSSCs.  $^{10\text{-}17}$  As the most important members of sensitizer family, Ru-complexes and porphyrinbased dyes have experienced a striking development and of which the representative dyes have achieved very high photoelectric conversion efficiency (PCE), such as 11% for N719,<sup>18</sup> 13% for SM315.<sup>19</sup> While the envisionable environmental stress for heavy-metal contained dyes and synthetic difficulties for porphyrin-based ones will inevitably hamper the prospect of their future development. Metal-free organic dyes have, therefore, attracted increasing interests because of the advantages of their rich skeleton and good flexibility on tailoring molecular structure.<sup>20-25</sup>

Similar to porphyrin-based dyes, the structure of organic dyes commonly adopt the donor– $\pi$ -bridge–acceptor (D– $\pi$ –A) configuration, since it is beneficial to facilitate intramolecular charge transfer (ICT) from donor to electron acceptor.<sup>26-32</sup> To extend the relatively narrow spectral response of organic dyes, decorating the main structure with conjugate unit is generally needed to enhance its light absorption and thus gain

promoted photocurrent.<sup>33-35</sup> Cyanoacrylic acid, which possesses a conjugate structure and strong electronwithdrawing feature, has consequently been employed as the electron acceptor and anchoring group to fabricate the most of metal-free organic dyes, replacing the benzoic acid which is successfully used in porphyrin-based dyes.<sup>36-39</sup> Another effective approach for expanding the conjugate system, broadening the absorption spectrum, and obtaining improved short-circuit current density ( $J_{sc}$ ) was also realized by the interposition of ethynyl unit between the donor and acceptor.<sup>40</sup> Apart from the  $J_{sc}$ , open-circuit voltage ( $V_{oc}$ ) is another critical factor that should be involved in the initial molecular design for achieving high device efficiency. Without the assistance of high  $V_{ocr}$ , many dyes with very high  $J_{sc}$  resulted in a low to moderate device efficiency.<sup>41-45</sup>

On this background, four novel triazatruxene-based organic dyes **JY43–46** featuring carboxylic acid/cyanoacrylic acid groups as electron acceptors and anchoring groups have been synthesized. Triazatruxene was applied for its strong electron donating ability in our early work,<sup>46</sup> and ethynyl unit was introduced in some of the target dyes to modify their conjugate structure. The photophysical, electrochemical, and photovoltaic properties of **JY43–46** were systematically investigated. The highest PCE of 7.51% was achieved based on dye **JY43** containing an inserted ethynyl unit and benzoic acid electron acceptor which seldom appears in metal-free organic dye molecules. The molecular structures of four dyes are shown in Fig. 1.

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Fig. 1 Molecular structures of dyes JY43-46.

## 2. Experiments

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#### 2.1. Materials and instruments

All chemicals were used as received unless otherwise stated. Dry THF and toluene were distilled over sodium with benzophenone indicator under nitrogen. DCM was distilled over calcium hydride. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker 400 MHz spectrometer. High resolution mass spectrometry (HRMS) data were recorded with a Varian 7.0T FTMS system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were recorded on an electrochemical workstation (Zennium, Zahner Corporation). CV experiments were performed in dry DCM with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) as supporting electrolyte, using a classical three-electrode system with a glassy carbon working electrode, a Ag/Ag<sup>+</sup> reference electrode, and a Pt wire counter electrode.

### 2.2. Fabrication and characterization of DSSCs

The double layer TiO<sub>2</sub> (8  $\mu$ m + 4  $\mu$ m) was printed on a FTO conducting glass by using a screen-printed technique. The transparent layer and scattering layer were coated by the commercial TiO<sub>2</sub> particles (Heptachroma Corporation) 20 nm and 200 nm, respectively. The  $TiO_2$  photoanodes were then heated gradually up to 500 °C and kept for 40 min at that temperature. After that, TiO<sub>2</sub> photoanodes were immersed into TiCl<sub>4</sub> aqueous solution (40 mM) at 70 °C for 40 min and sintered once again at 500 °C for 40 min. The Pt counter electrode was prepared by spin-coating one drop of 20 mM H<sub>2</sub>PtCl<sub>6</sub> solution in isopropyl alcohol on the surface of FTO conducting glass and subsequently heated to 400 °C and kept for 20 min. The TiO<sub>2</sub> photoanodes were immersed into a 0.3 mM solution of dyes with 5.0 mM chenodeoxycholic acid (CDCA) in THF at room temperature for 12 h. The N719 dye was immersed into a 0.3 mM solution in ethanol for 12 h. The liquid electrolyte was composed of 0.1 M Lil, 0.05 M I<sub>2</sub>, 0.5 M 4-tert-butylpyridine (TBP), 0.1 M guandine thiocyanate (GuSCN) and 0.6 M 1-propyl-3-methylimidazolium iodide (PMII) in acetonitrile. The photocurrent-voltage (J-V) characteristic curves of the DSSCs were measured under AM 1.5G simulated solar light using a Zennium electrochemical

workstation (Zahner Corporation). The incident photon-tocurrent conversion efficiency (IPCE) was measured using a commercial IPCE system (QTest Station 2000, CrownTech Corporation, USA). The DSSCs were fabricated into a sandwichtype structure and illuminated by a solar simulator (CHF-XM-500W, Trusttech Co. Ltd.) under 100 mW cm<sup>-2</sup> irradiation, which was calibrated by a standard silicon solar cell (91150V, Newport Corporation).

## 2.3. Synthesis

2.3.1. Synthesis of compound 2. To a 100 mL two-neck round bottom flask, triazatruxene (1) (345 mg, 1.0 mmol), t-BuOK (672 mg, 6.0 mmol) and 20 mL THF were added, the resultant mixture was heated under reflux for 0.5 h and n- $C_8H_{17}Br$  (1.0 mL, 6.0 mmol) was then added dropwise. After overnight reflux, reaction mixture was cooled to room temperature, diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified petroleum by column chromatography using ether/dichloromethane (10:1) as the eluent to give compound **2** (67% yield), a pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 0.79 - 0.87 (t, J = 6.7 Hz, 9H), 1.10 - 1.39 (m, 30H), 1.93 - 2.05 (t, J = 7.7 Hz, 6H), 4.88 – 4.96 (t, J = 7.9 Hz, 6H), 7.30 – 7.38 (t, J = 7.6 Hz, 3H), 7.41 - 7.49 (t, J = 7.6 Hz, 3H), 7.60 - 7.68 (d, J = 8.1 Hz, 3H), 8.25 – 8.34 (d, J = 8.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz,  $\mathsf{CDCl}_3)$   $\delta$  14.1, 22.6, 26.7, 29.1, 29.2, 29.8, 31.7, 47.0, 103.1, 110.5, 119.6, 121.5, 122.6, 123.5, 138.9, 140.9. HR-MS (MALDI):  $m/z [M]^{+}$  calcd for  $C_{48}H_{63}N_3$ , 681.5022; found, 681.5018.

**2.3.2.** Synthesis of compound **3.** In a 100 mL round bottom flask, compound **2** (500 mg, 0.73 mmol) was dissolved in 40 mL dichloromethane and cooled with an ice-water bath. To the mixture, a solution of *N*-bromosuccinimide (NBS) (131 mg, 0.73 mmol) in 5 mL DMF was then added dropwise. After that, the reaction was warmed to room temperature and stirred for 2 h. The mixture was diluted with dichloromethane, and washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude product compound **3** was directly used for next step.

2.3.3. Synthesis of compound 4. In a 100 mL two-neck round bottom flask, compound 3 (400 mg, 0.53 mmol), trimethylsilylacetylene (0.30 mL, 2.12 mmol), CuI (21 mg, 0.11 mmol), Pd(dppf)Cl<sub>2</sub> (110 mg, 0.15 mmol) were dissolved in 15 mL THF and 15 mL NEt<sub>3</sub>. The mixture was heated at 60 °C overnight under nitrogen. The mixture was subsequently diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography using petroleum ether/dichloromethane (6:1) as the eluent to give compound 4 (83% yield), a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.38 (s, 9H), 0.81 – 0.93 (m, 9H), 1.14 - 1.38 (m, 30H), 1.89 - 2.04 (m, 6H), 4.73 - 4.97 (m, 6H), 7.32 - 7.38 (t, J = 7.6 Hz, 2H), 7.43 - 7.50 (t, J = 7.6 Hz, 3H), 7.58 – 7.66 (m, 2H), 7.69 – 7.77 (d, J = 11.4 Hz, 1H), 8.12 – 8.18 (d, J = 8.4 Hz, 1H), 8.23 - 8.31 (m, 2H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 0.2, 14.1, 22.6, 26.6, 29.1, 29.7, 31.7, 46.9, 70.9, 93.0, Published on 05 February 2018. Downloaded by University of Windsor on 05/02/2018 12:53:04

103.0, 103.3, 106.8, 110.5, 113.8, 116.5, 119.7, 121.0, 121.5, 122.8, 123.3, 123.6, 123.7, 138.5, 138.8, 139.2, 139.6, 140.3, 140.9. HR-MS (MALDI): m/z  $[M]^+$  calcd for  $C_{53}H_{71}N_3Si$ , 777.5417; found, 777.5418.

2.3.4. Synthesis of compound 5. To a 100 mL round bottom flask with the solution of compound 4 (330 mg, 0.42 mmol) in 30 mL dry THF, TBAF (329 mg, 1.26 mmol) were added. After stirring at room temperature for half an hour, the mixture was diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude product was transferred into a 100 mL two-neck round bottom flask, and compound 10 (219 mg, 0.63 mmol), AsPh<sub>3</sub> (257 mg, 0.84 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (77 mg, 0.08 mmol), 15 mL THF, and 15 mL NEt<sub>3</sub> were successively added into the flask. The mixture was heated at 60 °C overnight under nitrogen, then cooled to room temperature and diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography using dichloromethane as the eluent to give compound 5 (55% yield, two steps), a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.78 – 0.89 (m, 9H), 1.10 – 1.38 (m, 30H), 1.86 - 2.10 (t, J = 8.2 Hz, 6H), 3.98 (s, 3H), 4.79 - 5.01 (m, 6H), 7.31 - 7.38 (td, J = 7.6, 2.6 Hz, 2H), 7.43 - 7.49 (t, J = 7.5 Hz, 2H), 7.49 - 7.55 (dd, J = 8.1, 6.5 Hz, 1H), 7.60 - 7.67 (m, 3H), 7.70 - 7.77 (m, 2H), 7.91 (s, 1H), 8.03 - 8.09 (m, 2H), 8.18 - 8.23 (m, 2H), 8.24 - 8.29 (dd, J = 10.0, 2.9 Hz, 2H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.1, 22.5, 26.6, 29.2, 29.8, 31.7, 47.0, 52.2, 84.9, 98.7, 103.0, 103.2, 103.4, 110.5, 113.8, 115.9, 117.4, 119.8, 121.2, 121.5, 122.9, 123.3, 123.8, 124.1, 128.3, 129.1, 129.4, 129.8, 131.5, 132.2, 132.4, 132.7, 138.5, 139.3, 139.8, 140.4, 140.9, 141.3, 152.9, 155.3, 166.8. HR-MS (MALDI): m/z  $[M]^{+}$  calcd for C<sub>64</sub>H<sub>71</sub>N<sub>5</sub>O<sub>2</sub>S, 973.5328, found, 973.5325.

2.3.5. Synthesis of compound 6. The compound 6 was synthesized using the same procedure for compound 5 except replacing compound 10 with compound 11. The residue was purified by column chromatography using dichloromethane as the eluent to give compound 6 (52% yield, two steps), a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.80 – 0.88 (m, 9H), 1.17 – 1.33 (m, 30H), 1.94 - 2.06 (m, 6H), 4.84 - 4.96 (m, 6H), 7.32 -7.37 (t, J = 7.3 Hz, 2H), 7.44 - 7.51 (t, J = 7.6 Hz, 2H), 7.61 -7.66 (m, 3H), 7.71 – 7.74 (d, J = 7.2 Hz, 1H), 7.88 – 7.91 (d, J = 5.1 Hz, 2H), 7.99 - 8.03 (d, J = 7.7 Hz, 2H), 8.11 - 8.15 (d, J = 7.6 Hz, 2H), 8.21 – 8.30 (dd, J = 12.8, 8.4 Hz, 3H), 10.09 (s, 1H). <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3)$   $\delta$  14.0, 22.6, 26.6, 29.1, 29.7, 31.7, 47.0, 84.9, 99.0, 103.0, 103.2, 103.4, 110.5, 110.6, 113.8, 115.8, 117.7, 119.8, 121.2, 121.5, 122.9, 123.3, 123.8, 124.1, 128.4, 129.7, 129.9, 132.3, 135.8, 138.5, 139.3, 139.8, 140.4, 140.9, 142.8, 152.8, 155.3, 191.8. HR-MS (MALDI): m/z [M]<sup>†</sup> calcd for  $C_{63}H_{69}N_5OS$ , 943.5223, found, 943.5220.

**2.3.6. Synthesis of compound 7.** In a 100 mL two-neck round bottom flask, compound **3** (500 mg, 0.66 mmol), bis(pinacolato)diboron (335mg, 1.32 mmol), potassium acetate (206mg, 2.10 mmol), Pd(dppf)Cl<sub>2</sub> (57mg, 0.07 mmol) were dissolved in 30 mL 1,4-dioxane. The mixture was heated at 90 °C overnight under nitrogen, then cooled to room

temperature, diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography using petroleum ether/dichloromethane (3:1) as the eluent to give compound 7 (78% yield), a pale yellow oil. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.84 - 0.95 (m, 9H), 1.16 - 1.44 (m, 30H), 1.51 (s, 12H), 1.94 - 2.14 (m, 6H), 4.90 - 4.96 (m, 4H), 5.01 - 5.07 (t, J = 7.8 Hz, 2H), 7.34 - 7.43 (q, J = 7.3 Hz, 2H), 7.45 - 7.54 (t, J = 7.6 Hz, 2H), 7.63 -7.69 (d, J = 8.1 Hz, 2H), 7.84 - 7.94 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 8.29 – 8.38 (t, J = 8.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.6, 24.9, 26.5, 26.9, 29.1, 29.7, 29.9, 31.7, 46.9, 83.7, 103.1, 110.5, 116.9, 119.7, 120.7, 121.4, 121.6, 122.7, 123.3, 123.5, 125.9, 138.8, 139.3, 139.6, 140.5, 140.9. HR-MS (MALDI):  $m/z [M]^{+}$  calcd for  $C_{54}H_{74}BN_{3}O_{2}$ , 807.5874, found, 807.5878.

2.3.7. Synthesis of compound 8. In a 100 mL round bottom flask, compound 7 (260 mg, 0.32 mmol), compound 10 (93 mg, 0.27 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) were dissolved in 20 mL THF and 5 mL  $K_2CO_3$  (2 M). The mixture was heated at 60 °C for 8 h under nitrogen, then cooled to room temperature, diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography using petroleum ether/dichloromethane (1:1) as the eluent to give compound 8 (90% yield), a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.73 – 0.91 (m, 9H), 1.08 - 1.42 (m, 30H), 1.93 - 2.16 (m, 6H), 3.99 (s, 3H), 4.84 - 5.05 (m, 6H), 7.31 - 7.39 (t, J = 7.7 Hz, 2H), 7.43 - 7.51 (d, J = 7.7 Hz, 2H), 7.61 - 7.68 (d, J = 8.2 Hz, 2H), 7.84 - 7.92 (t, J = 8.2 Hz, 2H), 7.93 - 7.99 (d, J = 7.6 Hz, 1H), 8.07 - 8.13 (d, J = 8.0 Hz, 2H), 8.20 - 8.26 (d, J = 8.1 Hz, 2H), 8.27 - 8.33 (t, J = 7.5 Hz, 2H), 8.35 - 8.41 (d, J = 7.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.6, 26.7, 29.1, 29.7, 31.7, 46.9, 52.2, 103.1, 110.4, 111.8, 119.7, 120.7, 121.5, 122.8, 123.3, 123.4, 123.7, 128.4, 128.6, 128.8, 129.1, 129.6, 129.8, 131.2, 131.3, 131.5, 132.2, 132.3, 134.8, 138.7, 139.2, 139.8, 140.8, 140.9, 141.2, 141.9, 154.0, 154.4, 166.9. HR-MS (MALDI): m/z [M]<sup>+</sup> calcd for C<sub>62</sub>H<sub>71</sub>N<sub>5</sub>O<sub>2</sub>S, 949.5328, found, 949.5325.

2.3.8. Synthesis of compound 9. The compound 9 was synthesized according to the same procedure for compound 8 except using compound 11 instead of compound 10. The residue was purified by column chromatography using dichloromethane as the eluent to give compound 6 (84% yield), a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.79 – 0.91 (m, 9H), 1.10 - 1.36 (m, 30H), 1.89 - 2.11 (q, J = 7.8 Hz, 6H), 4.78 -5.00 (m, 6H), 7.31 - 7.39 (t, J = 7.6 Hz, 2H), 7.43 - 7.51 (t, J = 7.7 Hz, 2H), 7.59 – 7.67 (m, 3H), 7.69 – 7.76 (d, J = 7.3 Hz, 1H), 7.86 - 7.93 (d, J = 5.7 Hz, 2H), 7.97 - 8.06 (d, J = 7.8 Hz, 2H), 8.09 - 8.16 (d, J = 7.8 Hz, 2H), 8.20 - 8.30 (dd, J = 13.1, 8.1 Hz, 3H), 10.09 (s, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.1, 22.6, 26.6, 29.1, 29.9, 31.7, 46.9, 102.9, 103.1, 103.2, 110.4, 110.5, 111.8, 119.7, 120.6, 121.4, 121.5, 122.8, 123.3, 123.8, 127.5, 129.0, 129.7, 129.9, 130.7, 131.1, 135.0, 135.6, 138.7, 139.1, 139.8, 140.8, 140.9, 141.1, 143.4, 153.9, 154.3, 191.9. HR-MS (MALDI):  $m/z [M]^+$  calcd for  $C_{61}H_{69}N_5OS$ , 919.5223, found, 919.5220.

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2.3.9. Synthesis of dye JY43. To a 100 mL round bottom flask with the solution of compound 5 (300 mg, 0.31 mmol) in 30 mL THF, 20 mL MeOH and a solution of 10 mL 20% NaOH(aq) was added. The mixture was stirred overnight at room temperature, then diluted with dichloromethane, washed with water and 1M HCl (aq). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography using dichloromethane/methanol (15:1) as the eluent to give dye JY43 (78% yield), a red solid, mp 179-181 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>/CDCl<sub>3</sub>, v/v = 10:1) δ 0.65 – 0.75 (m, 9H), 0.93 – 1.13 (m, 30H), 1.73 - 1.84 (m, 6H), 4.87 - 5.01 (m, 6H), 7.29 -7.34 (t, J = 7.2 Hz, 2H), 7.40 - 7.46 (t, J = 7.6 Hz, 2H), 7.54 -7.58 (d, J = 8.5 Hz, 1H), 7.73 - 7.78 (d, J = 8.0 Hz, 2H), 7.93 -7.96 (d, J = 7.4 Hz, 1H), 7.98 - 8.03 (d, J = 9.3 Hz, 2H), 8.09 -8.16 (q, J = 8.7 Hz, 4H), 8.21 – 8.27 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  13.8, 21.9, 25.6, 28.3, 28.8, 30.9, 46.1, 85.4, 97.8, 102.6, 102.7, 102.9, 111.2, 113.8, 115.5, 116.1, 119.9, 121.3, 122.4, 123.1, 123.3, 123.5, 128.5, 129.2, 129.5, 130.5, 131.9, 132.6, 137.7, 138.6, 139.1, 140.1, 140.5, 152.3, 154.6, 167.0. HR-MS (MALDI): m/z [M]<sup>+</sup> calcd for C<sub>63</sub>H<sub>69</sub>N<sub>5</sub>O<sub>2</sub>S, 959.5172, found, 959.5170.

2.3.10. Synthesis of dye JY44. In a 50 mL round bottom flask, compound 6 (160 mg, 0.17 mmol), cyanoacetic acid (71 mg, 0.85 mmol), NH<sub>4</sub>OAc (131 mg, 1.70 mmol) were dissolved in 10 mL acetic acid. The solution was heated to reflux for 6 h, then cooled to room temperature. diluted with dichloromethane, washed with water and brine. The organic layer was dried over anhydrous Na2SO4 and concentrated in vacuum. The residue was purified by column chromatography using dichloromethane/methanol (15:1) as the eluent to give dye **JY44** (80% yield), a red solid, mp 242–244 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>/CDCl<sub>3</sub>, v/v = 10:1) δ 0.61 – 0.78 (m, 9H), 0.90 – 1.18 (m, 30H), 1.65 - 1.88 (m, 6H), 4.75 - 5.07 (m, 6H), 7.28 -7.35 (m, 3H), 7.39 - 7.47 (m, 3H), 7.53 - 7.62 (m, 2H), 7.71 -7.80 (m, 2H), 7.93 – 7.99 (d, J = 8.4 Hz, 2H), 8.03 – 8.07 (d, J = 7.9 Hz, 2H), 8.11 - 8.17 (m, 2H), 8.20 - 8.26 (d, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  13.6, 21.9, 25.6, 28.3, 28.9, 29.0, 30.9, 31.1, 46.0, 85.2, 97.8, 102.5, 102.8, 110.6, 113.5, 115.5, 116.1, 118.3, 119.6, 121.0, 122.3, 122.7, 123.1, 127.9, 129.2, 129.5, 131.3, 131.7, 132.2, 132.8, 136.3, 137.6, 138.4, 138.5, 138.9, 140.3, 146.2, 147.8, 152.2, 154.6. HR-MS (MALDI):  $m/z [M]^{+}$  calcd for  $C_{66}H_{70}N_6O_2S$ , 1010.5281, found, 1010.5278.

**2.3.11. Synthesis of dye JY45**. The dye **JY45** was synthesized as the same procedure for dye **JY43**. The residue was purified by column chromatography using dichloromethane/methanol (15:1) as the eluent to give dye **JY45** (66% yield), a red solid, mp 157–158 °C. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  0.62 – 0.75 (m, 9H), 0.97 – 1.11 (m, 30H), 1.75 – 1.90 (m, 6H),

4.87 – 4.97 (m, 6H), 7.27 – 7.33 (t, J = 7.4 Hz, 2H), 7.39 – 7.45 (t, J = 6.9 Hz, 2H), 7.69 – 7.76 (m, 2H), 7.88 – 7.92 (d, J = 8.2 Hz, 1H), 7.95 – 7.99 (d, J = 7.4 Hz, 1H), 8.01 – 8.05 (d, J = 7.4 Hz, 1H), 8.09 – 8.15 (m, 4H), 8.20 – 8.30 (m, 3H), 8.46 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  13.6, 21.8, 25.7, 28.3, 28.9, 30.9, 46.0, 102.5, 102.6, 102.7, 110.8, 111.7, 119.7, 120.7, 121.0, 122.4, 122.5, 122.7, 122.8, 127.7, 128.8, 128.9, 129.3, 130.1, 130.3, 130.9, 133.5, 137.8, 138.3, 138.9, 140.4, 140.5, 140.6, 141.0, 153.4, 153.6, 167.0 HR-MS (MALDI): m/z [M]<sup>+</sup> calcd for C<sub>61</sub>H<sub>69</sub>N<sub>5</sub>OS, 935.5172, found, 935.5170.

**2.3.12. Synthesis of dye JY46**. The dye **JY46** was synthesized as the same procedure for dye **JY44**. The residue was purified by column chromatography using dichloromethane/methanol (15:1) as the eluent to give dye **JY46** (63% yield), a red solid, mp 258–260 °C. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  0.61 – 0.79 (m, 9H), 0.91 – 1.26 (m, 30H), 1.68 – 1.89 (m, 6H), 4.69 – 4.96 (m, 6H), 7.22 – 7.31 (m, 2H), 7.33 – 7.42 (d, J = 6.8 Hz, 2H), 7.52 – 7.61 (m, 1H), 7.64 – 7.72 (m, 1H), 7.78 – 7.84 (m, 1H), 7.87 – 7.95 (m, 2H), 7.98 – 8.04 (m, 2H), 8.07 – 8.27 (m, 6H), 8.37 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ /CDCl<sub>3</sub>, v/v = 10:1)  $\delta$  13.6, 21.9, 25.8, 28.4, 29.0, 30.9, 46.0, 102.3, 110.3, 119.4, 119.5, 120.4, 120.7, 120.9, 122.4, 122.6, 122.7, 127.3, 128.3, 129.1, 129.3, 129.7, 130.0, 130.8, 132.0, 133.6, 137.7, 138.2, 138.8, 140.1, 140.3, 153.6. HR-MS (MALDI): m/z [M]<sup>+</sup> calcd for C<sub>64</sub>H<sub>70</sub>N<sub>6</sub>O<sub>2</sub>S, 986.5281, found, 986.5278.

## 3. Results and discussion

### 3.1. Synthesis

The synthetic routes of dyes JY43-46 are displayed in Scheme 1. The intermediates  $\mathbf{1}$ ,  $\mathbf{10}^{19}$  and  $\mathbf{11}^{48}$  were prepared according to previous literatures. Compound 2 was obtained by the alkylation of the intermediate 1, and then functionalized with NBS to give bromo-substituted compound 3, which was subsequently transformed into compounds 4 and 7 via coupling reaction with trimethylsilylacetylene and bis(pinacolato)diboron, respectively. The deprotection of compound 4 was performed with tetrabutylammonium fluoride (TBAF) in THF, and the resulting terminal alkyne was subsequently reacted with compound 10/11 via Sonogashira cross-coupling to yield dye precursor compounds 5 and 6, respectively. The other precursor compounds 8 and 9 were obtained through Suzuki cross-coupling of intermediate 7 with compound 10 and 11, respectively. Further hydrolysis of ester compounds 5 and 8 gave the target dyes JY43 and JY45, respectively. Dyes JY44 and JY46 containing cyanoacrylic acid acceptor were synthesized by the classic Knoevenagel condensation reaction.

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Scheme 1 Synthetic routes for dyes JY43-46.

## 3.2. Optical and electrochemical properties

The UV-vis absorption spectra of the four triazatruxene based organic dyes in dichloromethane solutions and on  $TiO_2$  films are displayed in Fig. 2. The optical and electrochemical properties data are summarized in Table 1. In dichloromethane solutions, all of the four dyes exhibit two distinct absorption bands at 350-400 and 400-600 nm. The high-energy absorption bands below 400 nm can be attributed to  $\pi$ - $\pi$ \* transitions. The low-energy region at 400–600 nm can be assigned to the intramolecular charge transfer (ICT) from triazatruxene donor to electron acceptors.49 The maximum absorption peak of JY43 with carboxylic acid as the anchoring group/electron acceptor appears at 469 nm, 12 nm red-shift has been observed for dye JY44 replacing carboxylic acid by cyanoacrylic acid which features a conjugated structure and stronger electron-withdrawing ability. For the same reason, more significant red-shift (33 nm) has also been found for JY46 relative to JY45. The incorporation of acetylene between triazatruxene donor and BDT moiety is also in favor of the expansion of the dyes' conjugated structure, causing redshifted onset absorption of JY43 relative to JY45 at visible region. When adsorbed on TiO<sub>2</sub> films, as shown in Fig. 2b, the absorption ranges of dyes JY43-46 are broadened compared to the corresponding absorption spectra in solution, which is favorable for harvesting solar light.





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DOI: 10.1039/C7NJ04629D Journal Name



Fig. 3 Cyclic voltammetry curves for JY43-46 are recorded in DCM.

Cyclic voltammetry assessment was carried out in a classical three-electrode system in dicholoromethane to survey the redox behavior and standardized by  $Fc/Fc^{+}$  (0.63 V vs. NHE) with 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte.<sup>50</sup> The cyclic voltammetry curves for JY43-46 are shown in Fig. 3 and the pertinent data are displayed in Table 1. The first oxidation potential (E<sub>ox</sub>) of JY43-46 are 0.94, 0.99, 0.89 and 0.93V (vs. NHE), respectively, which is corresponding to the highest occupied molecular orbital (HOMO). Clearly, the HOMO levels of JY43 and JY44 are more positive than that of JY45 and JY46, respectively, mainly originated by the presence of an additional ethynyl unit. After employing electron-withdrawing cyanoacrylic acid as electron acceptor, the HOMO levels of JY44 and JY46 were both slightly shifted downward in comparison to JY43 and JY45, respectively. As a result, the dye JY44 containing both ethynyl unit and cyanoacrylic acid in skeleton shows the most positive HOMO level. The band gaps  $E_{0-0}$  of the dyes were calculated by  $E_{0-0}$  = 1240/ $\lambda_{int}$ , and the parameter  $\lambda_{int}$  were estimated by their onset wavelength in UV-absorption spectra.<sup>51</sup> Because of an obvious red-shift of absorption spectra, the  $E_{0-0}$  levels of JY44 (1.83 eV) and JY46 (1.82 eV) are more narrow than that of JY43 (2.06 eV) and JY45 (2.09 eV), respectively. The lowest unoccupied molecular orbital (LUMO) levels are calculated by  $E_{ox} - E_{0-0}$ ,<sup>52</sup> to be -1.12, -0.84, -1.20 and -0.89V (vs. NHE), respectively. The HOMO and LUMO levels matched well with iodine redox couples (0.4 V vs. NHE) and TiO<sub>2</sub> conduction band (-0.5 V vs. NHE), ensuring efficient dye regeneration and electron injection.

| Table 1 Optical and electrochemica | l properties of <b>JY43</b> - <b>46</b> <sup>a</sup> |
|------------------------------------|--|
|------------------------------------|--|

| Dye                  | $\lambda_{ m max}/ m nm$ | $\varepsilon/10^4~{\rm M}^{-1}$ | $\lambda_{\max}({ m on}$ | $E_{\rm ox}/V$ | $E_{0-0}/V$ | $E_{\rm red}/V$ |
|----------------------|--------------------------|---------------------------------|--------------------------|----------------|-------------|-----------------|
|                      |                          | cm <sup>-1</sup>                | TiO₂)/nm                 |                |             |                 |
| JY43                 | 469                      | 4.82                            | 471                      | 0.94           | 2.06        | -1.12           |
| JY44                 | 481                      | 3.35                            | 490                      | 0.99           | 1.83        | -0.84           |
| JY45                 | 464                      | 3.44                            | 477                      | 0.89           | 2.09        | -1.20           |
| JY46                 | 497                      | 2.95                            | 498                      | 0.93           | 1.82        | -0.89           |
| <sup>a</sup> The fir | st oxidation p           | otentials (E <sub>ox</sub> ) v  | were measure             | ed in DCM      | and calibra | ated with       |
| -                    |                          |                                 |                          |                |             |                 |

ferrocene (0.63 V vs. NHE);  $E_{0-0}$  was estimated from the intersection wavelength of normalized absorption spectra;  $E_{red} = E_{ox} - E_{0-0}$ .

#### 3.3. Theoretical calculations

To optimize the geometrical and electronic structure of the dye **JY43–46**, density functional theory (DFT) calculations were performed based on B3LYP/6-31G<sup>\*</sup> basis set with Gaussian 03 package.<sup>53</sup> The octyl group of dyes was replaced by methyl

group to save calculation time. The frontier molecular orbitals of the HOMOs and LUMOs of the four dyes are shown in Fig. 4. The optimized configurations exhibit that triazatruxene core has an axisymmetric rigid planar structure, which will promote electron distributed along the entire donor system. Apparently, the insertion of ethynyl unit between the triazatruxene donor and BTD moiety results in an extension of molecule conjugation and a slight improvement of molecule planarity. The dihedral angles between the donor and  $\pi$ -bridge of JY43 and JY44 are 25.3° and 28.5°, which is smaller than that of JY45 (36.5°) and JY46 (32.7°), respectively. More planarized conformation would be beneficial for obtaining electron delocalization and facilitating better the intramolecular electronic communication. It can be found that the HOMOs of all four dyes are mainly located on triazatruxene core and neighboring BTD unit, while the LUMOs are distributed on the carboxylic acid/cyanoacrylic acid acceptors and partly extended to BTD moieties. As a consequence, such electronic distribution of dyes is beneficial for charge transfer from the excited dyes to the TiO<sub>2</sub> conduction band.



Fig. 4 The frontier molecular orbital optimized of JY43-46 at the B3LYP/6-31G\* level.

## 3.4. Photovoltaic performance

The photovoltaic performances and parameters of the DSSCs have been determined under a simulated AM 1.5G irradiation  $(100 \text{ mW cm}^{-2})$  with iodine redox electrolyte consisting of 0.1 M LiI, 0.05 M I\_2, 0.5 M TBP, 0.1 M GuSCN and 0.6 M PMII in acetonitrile, and the active area of the cells is 0.196 cm<sup>2</sup>. The photocurrent density-voltage (J-V) curves of the dyes are plotted in Fig. 5a, and detailed photovoltaic data are summarized in Table 2. The dyes JY43 and JY44 show higher J<sub>sc</sub> values relative to dyes JY45 and JY46, respectively, indicating that the extended conjugate structure aroused by inserting acetylene group endows dyes JY43 and JY44 more efficient light absorption ability. Similar as that, in comparison to dyes JY43 and JY45, respectively, cyanoacrylic acid acceptor with larger conjugate structure against simple carboxyl acid acceptor makes dyes JY44 and JY46 an obvious Jsc improvement. With respect to another important performance factor  $V_{oc}$ , dye molecules with single carboxyl acid acceptor seems beneficial to obtain higher  $V_{oc}$  in contrast with cyanoacrylic acid acceptor. To achieve the best device efficiency, a good balance between  $V_{oc}$  and  $J_{sc}$  should thus be carefully assessed in the structural design of dyes. Finally, the dye **JY43** with an ethynyl unit and a carboxyl as electron acceptor exhibited the highest PCE of 7.51% (a  $J_{sc}$  of 14.97 mA cm<sup>-2</sup>, a  $V_{oc}$  of 793 mV and a FF of 0.632), which was nearly reached about 91% PCE of the commercial **N719**-based cells.



Fig. 5 (a) The photocurrent-voltage (J-V) curves and (b) the IPCE spectra of DSSCs based on the four dyes.

In order to further investigate the different  $J_{sc}$  values of the four dyes, the incident photon-to-current conversion efficiency (IPCE) spectra for the DSSCs based on JY43-46 have been performed. As shown in IPCE spectra (Fig. 5b), all of these dyes exhibit a broad spectral response within 350-650 nm, especially JY44 and JY46 show a broader spectral response within 350-720 nm. The IPCE response of the four dyes is according with the trend of their UV-vis absorption spectral. The spectra onsets of JY43-46 are at 640, 670, 720 and 720nm, respectively. Obviously, the dye JY44-based cells give over 60% IPCE values from 380 to 630 nm, the result is also well agreed with the highest J<sub>sc</sub> value in photovoltaic measurements. Meanwhile, the dye JY45 has a lower J<sub>sc</sub> than the other three dyes, because of the weak IPCE response in wavelength ranges of 350-450 nm. The IPCE measurement is well explained the change trend of  $J_{sc}$  values among the four dyes.

| Table 2 Photovoltaic performance of JY43-46 using N72 | 19 as a reference |
|---|-------------------|
|---|-------------------|

| Dye  | Γ/nmol cm <sup>-2</sup> | V <sub>oc</sub> /mV | J <sub>sc</sub> /mA cm <sup>-2</sup> | FF/%           | PCE/%           |  |
|------|-------------------------|---------------------|--------------------------------------|----------------|-----------------|--|
| JY43 | 113                     | 793 ± 2             | $14.97 \pm 0.20$                     | 63.2 ± 0.7     | 7.51 ± 0.08     |  |
| JY44 | 135                     | 707 ± 2             | $16.45 \pm 0.06$                     | $61.5 \pm 0.4$ | $7.15 \pm 0.05$ |  |
| JY45 | 103                     | 775 ± 3             | $13.46 \pm 0.16$                     | 62.2 ± 0.2     | 6.50 ± 0.07     |  |
|      |                         |                     |                                      |                |                 |  |

| JY46 | 110 | 743 ± 4 | $15.89 \pm 0.10$ | $61.5 \pm 0.6$ | 7.26 ± 0.06 |
|------|-----|---------|------------------|----------------|-------------|
| N719 |     | 800 ± 6 | $16.49 \pm 0.31$ | $62.4 \pm 0.8$ | 8.23 ± 0.09 |

DOI: 10.1039/C7NJ04629D

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<sup>a</sup> The active area of the cells was 0.196 cm<sup>2</sup>; The electrolyte was composed of 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.5 M 4-*tert*-butylpyridine (TBP) 0.1 M GuSCN and 0.6 M 1-propy-3-methylimidazolium lodide (PMII) in acetonitrile;  $\Gamma$  represents the amount of dye loading on the TiO<sub>2</sub> electrode.

### 3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the dark to investigate the electron recombination effect of four dyes JY43-46 in DSSCs.<sup>54</sup> The EIS Nyquist plots and Bode phase plots are shown in Fig. 6 and the tests were performed in a frequency range from 0.1 Hz to 100 kHz under a bias of -0.75 V. The interfacial charge transfer resistances ( $R_{ct}$ ) at the TiO<sub>2</sub>/dyes/electrolyte interface is related to the larger semicircle section on the right of the Nyquist plots.<sup>55</sup> A larger radius of the semicircle means a larger resistance of the electron recombination, which is benefit for a higher value of  $V_{\rm oc}$  <sup>56</sup> As shown in Fig. 6a, the fitted  $R_{\rm ct}$ decreases in the order of JY43 (93  $\Omega$ ) > JY45 (74  $\Omega$ ) > JY46 (44  $\Omega$ ) > **JY44** (28  $\Omega$ ), and the trend is in good accordance with the order of V<sub>oc</sub> of **JY43** (793 mV) > **JY45** (775 mV) > **JY46** (743 mV) > JY44 (707 mV). Except the interfacial  $R_{ct}$ , the electron lifetime ( $\tau$ ) is another important parameter concerned with V<sub>oc</sub> values of DSSCs, the longer lifetime means the lower current of DSSCs in the dark and corresponds to the higher photovoltage values. The electron lifetime which can be calculated from the peak frequency (f) at lower frequency region in the Bode phase plots by using  $\tau = 1/(2\pi f)$ , is enhanced in the order of **JY44** (8.4 ms) < JY46 (14.0 ms) < JY45 (20.7 ms) < JY43 (25.6 ms). So the dye JY43-based cell has the highest Voc of 793 mV can be further explained.



Fig. 6 Electrochemical impedance spectra (a) Nyquist plots and (b) Bode phase plots for the DSSCs based on the four dyes measured at –0.75V bias in the dark.

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DOI: 10.1039/C7NJ04629D

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## 4. Conclusions

In summary, novel dyes JY43-46 based on triazatruxene donor were designed and synthesized for DSSCs. Special focus was set on the effects of ethynyl unit and different electron acceptors on the photovoltaic performance of metal-free organic dyes. The incorporation of ethynyl unit and cyanoacrylic acid in the dye structure has proved that they can obviously promote the light harvesting ability, and gain a higher J<sub>sc</sub>. Cyanoacrylic acid, which has been considered as the most powerful acceptor to fabricate organic dyes for highly efficient DSSCs, ensures dye JY46 a better PCE in comparison to JY45 with carboxylic acid electron acceptor. However, for dyes containing one inserted ethynyl unit, JY43 with a carboxylic acid acceptor seems more effective relative to JY44 with cyanoacrylic acid acceptor, because of its much higher  $V_{oc}$ value 793 mV (vs 707 mV for JY44). These results indicate there is no privileged structure which must be involved in the design of metal-free organic dye for highly efficient DSSCs, a structure taking account of the good balance between  $J_{sc}$  and  $V_{\rm oc}$  should be first considered.

## **Conflicts of interest**

There are no conflicts to declare.

## Acknowledgements

We are grateful to the National Natural Science Foundation of China (21572108) and Tianjin Natural Science Foundation (16JCYBJC16700) for their financial support.

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## Effects of ethynyl unit and electron acceptors on the performance of triazatruxene based dye-sensitized solar cells

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Effects of ethynyl unit and electron acceptors/anchors on the photovoltaic performance of triazatruxene-based organic dyes were systematically investigated.

