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# Cyclic thiourea functionalized dyes with binary $\pi$ -linkers: Influence of different $\pi$ -conjugation segments on the performance of dye-sensitized solar cells

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#### Abstract

A series of cyclic thiourea functionalized dyes containing binary  $\pi$ -linkers were synthesized and applied in the dye-sensitized solar cells. The only difference of these dyes is that one segment of the binary  $\pi$ -linkers is thiophene, *n*-hexylthiophene, thienothiophene, 3,4-ethylenedioxythiophene, and benzene, respectively. Among them, the dyes incorporating electron-rich thienothiophene or 3,4-ethylenedioxythiophene exhibit the broader absorption bands and higher molar extinction coefficients in the visible region, which can not only enhance the light-harvesting ability but also improve the short-circuit current density; on the other hand, the dyes bearing bulky n-hexylthiophene or 3,4-ethylenedioxythiophene can effectively suppress the intermolecular  $\pi$ - $\pi$  aggregation and electron recombination owing to larger steric hindrance, which is beneficial to increase the open-circuit voltage.

*Keywords:* Cyclic thiourea; Dye-sensitized solar cells; Binary  $\pi$ -linker; Thiophene; Thienothiophene; 3,4-Ethylenedioxythiophene

#### 1. Introduction

With the development of global economy, energy consumption is being in the high growth period, hence the shortage of energy sources will be a serious problem that humanity has to face. Once a technological breakthrough is achieved, solar energy will provide us with inexhaustible energy. Among various light-harvesting devices, dye-sensitized solar cells (DSSCs) have attracted increasing attention due to the features of low carbon, friendly to environment and easy fabrication [1-3]. As a key component of DSSC, the sensitizer affects the power conversion efficiency (PCE) because of its critical function in light harvesting and electron injection. To date, sensitizers based on ruthenium complexes have achieved the PCE of almost 12% [4-6]. However, the large scale application of ruthenium complexes has become a critical problem because of resource limitation and cumbrous purification [7]. To resolve these issues, metal-free organic dyes have been developed as alternative sensitizers, because they exhibit advantages such as low material cost, high molar extinction coefficients, facile modification and ease of purification [8]. In past decade, there is a consecutive performance advancement of organic dyes as a result of systematic molecular engineering [9]. To the best of our knowledge, DSSCs based on single organic sensitizer has reached the PCE of 10.65% [10-13].

Most organic dyes tend to be designed with a dipolar D- $\pi$ -A architecture, where the donor (D) pushes electron into the metal oxide via the  $\pi$ -conjugated linker and acceptor (A) [14-16]. Therefore, enormous efforts have been devoted toward the design and synthesis of the three parts. So far, acceptors have been dominated by 2-cyanoacrylic acid, but various donors and linkers have been exploited. For example, hydrazone [17-19], carbazole [20-23], coumarin [24, 25], indoline [26, 27], phenothiazine [28, 29], phenoxazine [30], tetrahydroquinoline [31], and

triphenylamine [12, 23, 32-34] are widely adopted as donors. The main advantages of such compounds containing electron-rich nitrogen, oxygen, and sulfur heteroatoms are good electron-donating ability and rapid charge-transporting ability [17, 29, 33, 35]. To further improve device performance, a suitable  $\pi$ -conjugated linker is required between the donor and the acceptor based on the following consideration: (1) electron is easily transferred from the donor to the acceptor [16, 29]; (2) the absorption band could be broadened by the increase of the conjugation length [15, 36]; (3) the intermolecular aggregation can be suppressed by the steric hindrance of  $\pi$ -linkers [36-38]. Therefore, many kinds of electron-rich units have been introduced into the  $\pi$ -linkers, such as thiophene [20, 39-41], thienothiophene (TT) [12, 42, 43], and 3,4-ethylenedioxythiophene (EDOT) [8, 12].

In our previous studies [44, 45], the cyclic thiourea functionalized triphenylamine containing more nitrogen and sulfur heteroatoms was employed as an electron donor to construct dye molecules. Compared with triphenylamine-based dyes, such dyes exhibited better photophysical and photovoltaic performances. Moreover, the hexyl chains attached at the N-atom sites of cyclic thiourea groups contribute to suppress intermolecular aggregation and increase the solubility of dyes [22, 30]. Especially, the combination of cyclic thiourea functionalized triphenylamine as the donor and bithiophene (AZ6) or 3-hexyl-2, 2'-bithiophene (AZ261) as the  $\pi$ -linkers showed broader spectral ranges and reduced intermolecular aggregation. Our results demonstrate that the increased conjugation of  $\pi$ -linkers is beneficial to improve the photocurrent density due to the broad absorption band. Therefore, a further optimization is carried out by increase of the linker conjugation via the insertion of a election-rich fusing ring TT or a EDOT with a small torsion angle [12]. Three new organic dyes with different binary  $\pi$ -linkers were synthesized, which coded as AZ362

with TT, **AZ463** with EDOT, and **AZ564** with benzene (Fig. 1). Through density functional theory (DFT) calculations, we estimated these dyes have relatively small HOMO-LUMO energy gaps ( $E_g$ ), which is suitable for a wide spectral response [8]. Here, various  $\pi_1$  segments are inserted into the  $\pi$ -linkers, with a clear motivation to further investigate the impact of  $\pi$ -conjugation, geometry and electron-rich segment on photophysical, electrochemical and photovoltaic properties.

#### 2. Experimental section

#### 2.1. Materials and reagents

Thienothiophene (TT), 3,4-ethylenedioxythiophene (EDOT), 5-formyl-2-thiopheneboronic acid, N-bromosuccinimide (NBS), and Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Aladdin-reagent Co.. All chromatographic separations were carried out on silica gel (200-300 mesh). Transparent FTO conducting glass (fluorine doped SnO<sub>2</sub>, sheet resistance 15 $\Omega$ /square, transmission > 90% in the visible region) was obtained from Nippon Sheet Co., Ltd.. All the chemicals and solvents used in this work were of analytical grade and used without further purification unless otherwise stated.

#### 2.2. Characterizations

#### 2.2.1. Structure confirmation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AV-300 MHz or Bruker AV-400 MHz instruments with tetramethylsilane (TMS) as the internal standard. Gas chromatography mass spectra (GC-MS) were acquired in the electron ionization mode (EI) on Thermo DSQII. High resolution mass spectra (HRMS) were measured with a Bruker maXis mass spectrometer. Elemental analysis (C H N) was carried out on a VARIO-EL-III elemental analyzer.

#### 2.2.2. Photophysical measurements

UV-Vis absorption spectra of the dyes in MeCN-DCM (1:1, v/v, where MeCN is acetonitrile, and DCM is dichloromethane;  $1 \times 10^{-5}$  M) solutions and on the adsorbed TiO<sub>2</sub> films (6.5 µm) were measured with a Shimadzu UV-3600 spectrophotometer.

#### 2.2.3. Electrochemical measurements

Cyclic voltammograms (CV) were conducted on a CHI 660D Electrochemical Workstation at a scan rate 100 mV s<sup>-1</sup>, measured in a MeCN-DCM (3:1, v/v) solution containing 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) as a supporting electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: non-aqueous Ag/Ag<sup>+</sup> electrode) under argon atmosphere. The redox potentials were calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as the internal reference.

Electrical impedance spectra (EIS) under dark with bias -0.7 V were also measured with CHI 660D Electrochemical Workstation at frequencies of 0.05-100000 Hz. The magnitude of the alternative signal was 10 mV. Charge-transfer resistances were determined by fitting the impedance spectra using Z-view software.

#### 2.3. Theoretical calculations

The electronic configuration and geometry structure of the dyes were optimized by density functional theory (DFT) calculations with the Gaussian 03 program package at the B3LYP/6-311G(d, p) level.

#### 2.4. Fabrication and characterization of DSSCs

 $TiO_2$  films were prepared with a screen printing method according to the published method [45]. Then the films were immersed into a 0.4 mM dye bath in DCM solution under dark for 24 h at room temperature. The active area of the  $TiO_2$  photoanode film was approximately 0.25 cm<sup>2</sup>. All other fabrication processes of

DSSCs were also performed according to the published method [45].

Photocurrent-voltage (*J-V*) characteristics of the DSSCs were measured under illumination with AM 1.5 G solar light from a 300 W xenon lamp solar simulator (94022A, Newport Co., USA). The incident light intensity was calibrated to 100 mW cm<sup>-2</sup> with a standard silicon solar cell. *J-V* characteristics were recorded with a digital source meter (Keithley 2400) controlled by a computer. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were tested on a commercial setup (QTest Station 2000 IPCE Measurement System, Crowntech, USA).

#### 2.5. Synthesis

The synthetic procedures of AZ6 [44], AZ261 [45], and the starting material (4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)amino)phenyl)bo ronic acid (1) [45] have been reported in our previous papers, and the synthesis of intermediates 2a, 2b, and 2c can be found in the Supporting Information. The synthetic routes of AZ362, AZ463, and AZ564 are shown in Fig. 2, and the synthetic details are described as follows.

# 2.5.1. 5-(5-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5yl)amino)phenyl)thieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde (**3a**)

In a 100 mL 3-necked flask, compound 1 (700 mg, 0.90 mmol), 2a (330 mg, 1.0 mmol), tetra-*n*-butylammonium bromide (TBAB) (87 mg, 0.27 mmol), N, N-dimethylformamide (DMF) (50 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (12 mg, 0.01 mmol) were added in turn under a nitrogen atmosphere. Following this,  $K_2CO_3$  aqueous solution (0.18 mol L<sup>-1</sup>, 10 mL) was added dropwise. The reaction mixture was stirred for 2 h at 75 °C, and then poured into ethyl acetate (EA). The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the crude

product obtained was purified by column chromatography (PE/EA = 10/1, v/v; where PE is petroleum ether, boiling range: 60-90 °C) to give an orange semisolid (730 mg, 83% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.74 (s, 1H), 7.57 (d, *J* = 3.9 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.39 (s, 1H), 7.27 (s, 1H), 7.16 (d, *J* = 3.9 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.97-6.90 (m, 6H), 4.20 (t, *J* = 4.2 Hz, 4H), 4.10 (t, *J* = 4.2 Hz, 4H), 1.75-1.65 (m, 8H), 1.35-1.16 (m, 24H), 0.80 (t, *J* = 6.9 Hz, 6H), 0.73 (t, *J* = 6.0 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.25, 169.50, 148.36, 147.87, 147.36, 143.03, 141.62, 140.96, 138.49, 137.32, 136.53, 133.15, 128.87, 127.72, 126.72, 124.02, 121.92, 120.44, 118.39, 114.16, 109.64, 106.05, 44.92, 44.72, 31.47, 31.40, 27.93, 27.81, 26.57, 26.44, 22.54, 22.46, 14.01, 13.99. HRMS (ESI, *m*/z): [M+H]<sup>+</sup> calcd for (C<sub>55</sub>H<sub>68</sub>N<sub>5</sub>OS<sub>5</sub>): 974.4027, found: 974.4041.

2.5.2. 5-(7-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophene-2-carbaldehyde
(3b).

The synthesis method resembles that of compound **3a** but **2b** instead of **2a**, and the crude product obtained was purified by column chromatography (PE/EA = 8/1, v/v) to give an orange semisolid (760 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 9.73 (s, 1H), 7.56-7.52 (m, 3H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.95-6.87 (m, 6H), 4.34-4.27 (m, 4H), 4.19 (t, *J* = 6.0 Hz, 4H), 4.09 (t, *J* = 5.6 Hz, 4H), 1.74-1.73 (m, 4H), 1.65-1.63 (m, 4H), 1.34-1.17 (m, 24H), 0.80 (t, *J* = 6.0 Hz, 6H), 0.74 (t, *J* = 5.6 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.35, 169.37, 147.38, 144.82, 143.15, 140.76, 140.49, 137.66, 136.95, 133.10, 128.72, 127.19, 125.83, 122.68, 121.90, 120.35, 118.20, 109.60, 108.35, 105.91, 65.10, 64.65, 44.91, 44.70, 31.47, 31.41, 27.93, 27.81, 26.57, 26.44, 22.54, 22.46, 14.03, 14.01. HRMS (ESI, *m*/z): [M+H]<sup>+</sup> calcd for (C<sub>55</sub>H<sub>70</sub>N<sub>5</sub>O<sub>3</sub>S<sub>4</sub>): 976.4361; found: 976.4349. 2.5.3. 5-(4'-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5yl)amino)-[1,1'-biphenyl]-4-yl)thiophene-2-carbaldehyde (**3c**).

The synthesis method resembles that of compound **3a** but **2c** instead of **2a**, and the crude product obtained was purified by column chromatography (PE/DCM/MeOH = 40/20/1, v/v/v; where MeOH is methanol) to give a yellow semisolid (700 mg, 85% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.87 (s, 1H), 7.75-7.72 (m, 3H), 7.66 (d, J = 6.3Hz, 2H), 7.55 (d, J = 6.3Hz, 2H), 7.45 (d, J = 3.0 Hz, 1H), 7.13-7.10 (m, 4H), 7.04-7.01 (m, 4H), 4.29 (t, J = 4.8Hz, 4H), 4.20 (t, J = 5.1 Hz, 4H), 1.86-1.81 (m, 4H), 1.76-1.73 (m, 4H), 1.45-1.25 (m, 24H), 0.89 (t, J = 5.4 Hz, 6H), 0.82 (t, J = 5.4 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.62, 169.41, 153.86, 148.15, 143.31, 142.28, 141.37, 137.52, 133.22, 133.12, 131.49, 128.74, 127.66, 127, 04, 126.85, 123.95, 122.17, 120.40, 109.64, 105.97, 44.91, 44.70, 31.48, 31.41, 27.94, 27.81, 26.57, 26.43, 22.54, 22.46, 14.03, 13.99. HRMS (ESI, m/z): [M+H]<sup>+</sup> calcd for (C<sub>55</sub>H<sub>70</sub>N<sub>5</sub>OS<sub>3</sub>): 912.4742; found: 912.4745.

2.5.4. (E)-3-(5-(5-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (AZ362)

In a 100 mL 3-necked flask, compound **3a** (680 mg, 0.70 mmol), acetic acid (50 mL), cyanoacetic acid (150 mg, 1.75 mmol) and ammonium acetate (160 mg, 2.10 mmol) were added in turn under a nitrogen atmosphere. The reaction mixture was refluxed for 5 h. After cooling to room temperature, the mixture was poured into ice water. The precipitate was filtered, washed by distilled water, and purified by column chromatography (DCM/MeOH = 20/1, v/v) to give a dark red solid (480 mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.40 (s, 1H), 7.66 (d, *J* = 4.4 Hz, 1H), 7.51-7.48 (m, 3H), 7.36 (s, 1H), 7.25 (d, *J* = 4.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H),

7.06-6.99 (m, 6H), 4.27 (t, J = 7.2 Hz, 4H), 4.19 (t, J = 7.2 Hz, 4H), 1.85-1.82 (m, 4H), 1.76-1.72 (m, 4H),1.44-1.24 (m, 24H), 0.89 (t, J = 6.8 Hz, 6H), 0.82 (t, J = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 169.58, 167.06, 148.22, 147.60, 146.37, 142.90, 142.06, 140.87, 138.61, 136.71, 136.68, 134.89, 133.12, 128.85, 127.81, 126.65, 124.18, 121.87, 120.25, 118.16, 116.88, 114.10, 109.58, 105.98, 95.72, 44.93, 44.68, 31.48, 31.39, 27.95, 27.80, 26.58, 26.43, 22.55, 22.45, 14.03, 139.9. HRMS (ESI, m/z): [M-H]<sup>-</sup> calcd for (C<sub>58</sub>H<sub>67</sub>N<sub>6</sub>O<sub>2</sub>S<sub>5</sub>): 1039.3929; found: 1039.3920. Anal calcd for (C<sub>58</sub>H<sub>68</sub>N<sub>6</sub>O<sub>2</sub>S<sub>5</sub>): C, 66.88; H, 6.58; N, 8.07. Found: C, 66.91; H, 6.62; N, 8.00.

2.5.5. (E)-3-(5-(7-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (AZ463).

The synthesis method resembles that of **AZ362** but **3b** instead of **3a**, and the crude product obtained was purified by column chromatography (DCM/MeOH = 15/1, v/v) to give a dark purple solid (380 mg, 52% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.09 (s, 1H), 7.56-7.51 (m, 3H), 7.17 (d, *J* = 4.4 Hz, 1H), 6.99 (d, *J* = 6.0 Hz, 2H), 6.92-6.88 (m, 6H), 4.38-4.28 (m, 4H), 4.18 (t, *J* = 5.6 Hz, 4H), 4.10 (t, *J* = 5.6 Hz, 4H), 1.74-1.72 (m, 4H), 1.66-1.64 (m, 4H), 1.34-1.16 (m, 24H), 0.81 (t, *J* = 4.8 Hz, 6H), 0.74 (t, *J* = 4.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 168.37, 167.55, 146.57, 146.03, 145.84, 142.00, 140.56, 138.61, 138.48, 136.77, 132.10, 127.79, 126.22, 124.48, 122.31, 120.56, 119.45, 118.70, 115.31, 108.60, 107.31, 105.05, 93.55, 64.25, 63.62, 43.90, 43.72, 30.46, 30.40, 26.92, 26.81, 25.56, 25.43, 21.52, 21.45, 13.00, 12.99. HRMS (ESI, *m*/z): [M-H]<sup>-</sup> calcd for (C<sub>58</sub>H<sub>69</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>): 1041.4263; found: 1041.4252. Anal calcd for (C<sub>58</sub>H<sub>70</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>): C, 66.76; H, 6.76; N, 8.05. Found: C, 66.69; H, 6.70; N, 8.01.

2.5.6. (*E*)-3-(5-(4'-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5yl)amino)-[1,1'-biphenyl]-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (**AZ564**).

The synthesis method resembles that of **AZ362** but **3c** instead of **3a**, and the crude product obtained was purified by column chromatography (DCM/MeOH = 25/1, v/v) to give a purple solid (480 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.36 (s, 1H), 7.76-7.71 (m, 3H), 7.61 (d, J = 5.6 Hz, 2H), 7.51 (d, J = 6.0Hz, 2H), 7.42 (d, J = 4.0 Hz, 1H), 7.10-7.09 (m, 4H), 7.07-6.99 (m, 4H), 4.28 (t, J = 4.8Hz, 4H), 4.18 (t, J = 4.4 Hz, 4H), 1.85-1.80 (m, 4H), 1.74-1.71 (m, 4H), 1.45-1.24 (m, 24H), 0.89 (t, J = 4.8 Hz, 6H), 0.81 (t, J = 4.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 169.40, 167.89, 154.95, 148.21, 147.55, 143.26, 141.61, 140.06, 134.84, 133.13, 133.08, 131.10, 128.77, 127.66, 127.01, 126.96, 124.31, 122.12, 120.40, 116.13, 109.64, 105.99, 97.85, 44.94, 44.72, 31.48, 31.41, 27.95, 27.82, 24.82, 26.58, 26.44, 22.55, 22.46, 14.02, 13.99. HRMS (ESI, m/z): [M-H] <sup>-</sup> calcd for (C<sub>58</sub>H<sub>69</sub>N<sub>6</sub>O<sub>2</sub>S<sub>3</sub>): 977.4644; found: 977.4623. Anal calcd for (C<sub>58</sub>H<sub>70</sub>N<sub>6</sub>O<sub>2</sub>S<sub>3</sub>): C, 71.13; H, 7.20; N, 8.58. Found: C, 71.11; H, 7.17; N, 8.59.

#### 3. Results and discussion

#### 3.1. Synthesis and structural characterization

The synthesis of the three dyes (AZ362, AZ463, and AZ564) is extremely straightforward. As illustrated in Fig. 2, the target dyes were prepared by Suzuki coupling reaction and Knoevenagel condensation reaction. Suzuki coupling reaction of compound 1 and bromide (2a, 2b, or 2c) with  $Pd(PPh_3)_4$  as the catalyst in a mixture of K<sub>2</sub>CO<sub>3</sub> aqueous solution and DMF afforded the corresponding intermediates (3a, 3b, or 3c). Then, the target dyes were synthesized via Knoevenagel condensation reaction of aldehydes (3a, 3b, or 3c) with cyanoacetic acid in the presence of CH<sub>3</sub>COOH and CH<sub>3</sub>COONH<sub>4</sub>. All the intermediates and target dyes were confirmed by standard spectroscopic methods.

#### 3.2. Photophysical properties

The UV-Vis absorption spectra of the dyes in MeCN-DCM solutions and on  $TiO_2$ films are displayed in Fig. 3, and the corresponding photophysical data are listed in Table 1. As shown in Fig. 3a, all of the dyes exhibit two distinct absorption bands, one is from the local  $\pi$ - $\pi$ \* absorption in the UV region [23, 36] and the other arises from the intramolecular charge transfer (ICT) absorption in the visible region [29, 46]. It is noticeable that AZ564 with benzene as the  $\pi_1$  segment shows an overlap between the local  $\pi$ - $\pi$ \* absorption and the ICT absorption. Compared with AZ564, the other four dyes (AZ6, AZ261, AZ362, and AZ564) display broader absorption bands. This may be caused by the better delocalization of electron over the whole molecule when thiophene and its derivatives (*n*-hexylthiophene, TT, and EDOT) are used as the  $\pi_1$ segments compared to benzene [47, 48]. Compared with that of AZ6, the absorption spectrum of AZ261 is blue-shifted by 9 nm in the maximum absorption wavelength  $(\lambda_{\text{max}})$  together with a lower molar extinction coefficient ( $\varepsilon$ ), which could be attributed to large steric effect caused by *n*-hexyl chain attached to the thiophene unit. However, the absorption bands and molar extinction coefficients of AZ362 ( $\lambda_{max} = 488$  nm,  $\varepsilon =$ 37800 M<sup>-1</sup> cm<sup>-1</sup>) and AZ463 ( $\lambda_{max} = 504$  nm,  $\varepsilon = 39800$  M<sup>-1</sup> cm<sup>-1</sup>) are broader and intenser than those of AZ6 ( $\lambda_{max} = 475$  nm,  $\varepsilon = 31200$  M<sup>-1</sup> cm<sup>-1</sup>), which may demonstrate the superiority of TT and EDOT as the conjugation segments in light harvesting. It is well known that broader absorption band and higher molar extinction coefficient are favorable to the performance of DSSCs, as more photons can be harvested [40]. The absorption spectra of the dyes on 6.5 µm TiO<sub>2</sub> films are shown in Fig. 3b. The absorption spectra of all five dyes exhibit strong and broad absorption

bands. Especially, the absorption intensity from 400 to 650 nm are significantly enhanced, which could be explained by the increased delocalization of the  $\pi^*$  orbital of the conjugated skeleton caused by the interaction between the carboxylate group and the Ti<sup>4+</sup> ions, and the energy of the  $\pi^*$  level is directly decreased [40]. This is beneficial to harvest the visible light and thus increase the photocurrent response [46].

#### 3.3. Electrochemical properties

To investigate the feasibility of the electron injection from the excited dye to the conduction band of the TiO<sub>2</sub> electrode and dye regeneration via electron donation from the electrolyte [48], cyclic voltammetry (CV) was carried out and shown in Fig. 4. All of the dyes show oxidation/reduction processes at positive potential range and reduction/oxidation processes at negative potential range, indicating that these dyes have the capability to transport both electrons and holes [49]. The HOMO and LUMO energy levels ( $E_{\rm HOMO}$  and  $E_{\rm LUMO}$ ) as well as the electrochemical energy gap ( $E_z^{\rm ec}$ ) were calculated from the onset oxidation potentials ( $E_{\rm ox}$ ) and the onset reduction potentials ( $E_{\rm red}$ ) by assuming the energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) to be -4.72 eV below the vacuum level [50, 51]. The results are listed in Table 1. From these data, it is observed that all of the dyes have sufficiently high  $E_{\rm LUMO}$  and are energetically favorable for electron injection into the conduction band of TiO<sub>2</sub> (*ca.* -4.0 eV *vs.* vacuum [52]). The  $E_{\rm HOMO}$  also favors the regeneration of the oxidized dye by  $\Gamma/I_3^-$  redox couple (-4.80 eV *vs.* vacuum [53]).

#### 3.4. Theoretical calculations

To gain insight into the molecular structures and electron distribution, density functional theory (DFT) calculations were conducted using the Gaussian 03 program package at the B3LYP/6-311G(d, p) level, and the calculated results are also recorded in Table 1. As shown in Fig. 5, the HOMOs of the five dyes are mainly distributed

along the cyclic thiourea functionalized triphenylamine units and the  $\pi$ -linkers, and the LUMOs are delocalized across the linkers and the acceptors. Obviously, the HOMO and LUMO perfectly revealed that the donor-acceptor character of the cyclic functionalized triphenylamine thiourea and the anchoring groups. The well-overlapped HOMO and LUMO orbitals on the  $\pi$ -linker indirectly suggest the well inductive or withdrawing electron tendency from the donor to the acceptor. Such dye architecture provides an energy gradient for the excitation and facilitates the HOMO to LUMO charge transfer transition, which is crucial to afford a favorable energetic pathway for electron injection into the conduction band of TiO<sub>2</sub> [43]. In addition, it is worth noting that the  $E_g$  from the DFT calculations is bigger than the E from the experiments, which is a common feature of organic optoelectronic materials and may be related with the solvent effect [42, 54]; but the relationship between them is linear (Fig. 6).

Fig. 7 shows the optimized structure of the dyes. Dihedral angles between phenyl and  $\pi_1$  segment ( $\theta_1$ ) or  $\pi_1$  segment and adjacent thiophene ( $\theta_2$ ) are listed in Table 1. When different  $\pi_1$  segments are fixed to the horizontal plane, it can be seen that the geometries of  $\pi$ -linkers are greatly affected. Among these dyes, **AZ261** exhibits larger steric hindrance due to the introduction of the hexyl chain, but a more twisted dihedral angle between two thiophenes (20.33°) is found compared with that of **AZ6** (15.01°). This may weaken the ICT interactions, resulting in a blue shift of the maximum absorption band [37], which is consistent with the experimental observation in the absorption spectra. More interestingly, when bulky EDOT is employed to construct **AZ463**, the adjacent thiophene is rotated approximately 180°. It is worth noting that **AZ463** displays excellent molecular coplanarity. Apparently, such  $\pi$ -linker can show both large steric hindrance and conjugated coplanarity. Generally, large steric

hindrance can effectively suppress the intermolecular aggregation and charge recombination [37], while good molecular coplanarity can maximize the  $\pi$ -conjugation pathway throughout the whole molecule and bring a remarkably red shift in the maximum absorption band [43]. This indicates that it will probably exhibit better photovoltaic performances.

#### 3.5. Photovoltaic performance of DSSCs

Fig. 8 shows the IPCE spectra and *J-V* curves for DSSCs based on the five dyes. As seen from Fig. 8a, the DSSCs based on AZ6, AZ261, AZ362, and AZ463 display the maximum IPCE values of 79.65% at 490 nm, 81.76% at 480 nm, 85.33% at 500 nm, and 80.56% at 510 nm, respectively. And, the IPCE spectra of them cover in the region from 300 nm to 700 nm. The DSSC based on AZ564, by contrast, exhibits the smallest maximum IPCE value and narrowest IPCE spectrum. This indirectly indicates that thiophene, *n*-hexylthiophene, TT, and EDOT as the  $\pi_1$  segments can more efficiently convert the visible light into photocurrent. Generally, bigger integral of the IPCE spectrum means higher electron transfer yield [55], indicating that their cells would generate the higher conversion efficiency.

The photovoltaic performance parameters of DSSCs, including short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), and power conversion efficiency (PCE) are collected in Table 2, and the *J*-*V* curves are shown in Fig. 8b. As a core dye, **AZ6** yields a PCE of 7.18% ( $J_{sc} = 15.57 \text{ mA cm}^{-2}$ ,  $V_{oc} = 709.0 \text{ mV}$ , and FF = 0.65). At the same time, **AZ261** produces a slightly higher  $J_{sc}$  of 15.93 mA cm<sup>-2</sup> and a higher  $V_{oc}$  of 720.1 mV because of the introduction of hexyl chain, resulting in a PCE up to 7.46%. The improved  $J_{sc}$  of **AZ261** may be ascribed to its coplanar structure [40], while the enhanced  $V_{oc}$  may be attributed to the intermolecular  $\pi$ - $\pi$  aggregation and eletron recombination being suppressed by long hexyl chain attached

at the bithiophene linker. When the  $\pi_1$  segment changed from thiophene to TT or EDOT, the  $J_{sc}$  increases by 1.06 mA cm<sup>-2</sup> for **AZ362**, 0.79 mA cm<sup>-2</sup> for **AZ463**, respectively. This is because electrons could be more easily transferred from the donor into the TiO<sub>2</sub> film in the presence of electron-rich atoms (sulfur and oxygen) [56]. In addition, the broader range of light absorption for **AZ362** and **AZ463** may also contribute to the higher  $J_{sc}$  [8]. Nevertheless, the  $V_{oc}$  of **AZ362** decreases by 40.4 mV compared to that of **AZ6**, which might be due to the intermolecular  $\pi$ - $\pi$  aggregation. In contrast, the bulky character of the EDOT unit [8] in **AZ463** may effectively suppress the intermolecular aggregation [29, 57] and the electron recombination between the TiO<sub>2</sub> photoanode and the electrolyte, which can contribute to the higher  $V_{oc}$  and  $J_{sc}$ . Under the same measurement conditions, **AZ564** bearing benzene without electron-rich atoms as the  $\pi_1$  segment exhibits the lowest PCE of 6.25% with a  $J_{sc}$  as low as 12.76 mA cm<sup>-2</sup>, even though the highest  $V_{oc}$  is obtained.

#### 3.6. Electrochemical impedance spectroscopy

To further elucidate the photovoltaic results and obtain more interfacial charge transfer information, electrochemical impedance spectroscopy (EIS) was investigated.

In the Nyquist plots (Fig. 9a), there are two semicircles, and the larger semicircle indicates charge-transfer resistance ( $R_{rec}$ ) at the TiO<sub>2</sub>/dye/electrolyte interface; e.g., a larger radius indicates a larger  $R_{rec}$  and slower electron recombination. In the Bode phase plots (Fig. 9b), the lower-frequency peak is indicative of the charge-transfer process of injected electrons in TiO<sub>2</sub>, and the electron lifetime ( $\tau_e$ ) can be calculated from the peak frequency [47]. The calculated results increase in the order of **AZ362** (22.1 ms) < **AZ6** (25.2 ms) < **AZ463** (26.5 ms) < **AZ261** (29.2 ms) < **AZ564** (31.3 ms). Obviously, both the  $R_{rec}$  and  $\tau_e$  coincide well with  $V_{oc}$ . The enlarged  $R_{rec}$  and lengthened  $\tau_e$  further indicate that the electron recombination between the injected

electrons and the electrolyte was decreased, resulting in an increased  $V_{\rm oc}$  [47].

#### 4. Conclusions

In summary, five cyclic thiourea functionalized dyes with binary  $\pi$ -linkers are reported as sensitizers for DSSCs application. Our results reveal that the incorporation of electron-rich TT and EDOT as the  $\pi_1$  segments can facilitate electron transfer from the donor to the acceptor and realize the enhancement of light-harvesting ability, resulting in an increased  $J_{sc}$ . On the other hand, the introduction of bulky *n*-hexylthiophene and EDOT as the  $\pi_1$  segments can effectively suppress the intermolecular aggregation and charge recombination, which is beneficial for the improvement of  $V_{oc}$ . In addition, according to the optimized structure by DFT calculations, the combination of EDOT and thiophene as the  $\pi$ -linker makes **AZ463** show both larger steric hindrance and better conjugated coplanarity. Therefore, DSSC based on **AZ463** exhibits the best PCE of 7.68% ( $J_{sc} = 16.36$  mA cm<sup>-2</sup>,  $V_{oc} = 710.0$  mV, FF = 0.66). These results strongly indicate that selecting appropriate conjugation unit as the  $\pi$ -linker is a promising way to improve the performance of DSSCs.

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#### Table 1

Absorption, cyclic voltammetry (CV), and density functional theory (DFT) calculations of the

dyes.

| Dyes  | Absorption   |   | $\mathrm{CV}^c$ |                                      |                           |                           | $\mathrm{DFT}^d$                |                           |                           |                    |                          |                         |
|-------|--|---|-----------------|--------------------------------------|---------------------------|---------------------------|---------------------------------|---------------------------|---------------------------|--------------------|--------------------------|-------------------------|
|       | $\lambda_{\rm max}/{\rm nm}$<br>$(\varepsilon/{ m M}^{-1}~{ m cm}^{-1})^a$ | $\lambda_{\rm max}/{\rm nm} \ (\varepsilon/{ m M}^{-1}~{ m cm}^{-1})^b$ | $E_{\rm ox}$ V  | ${\scriptstyle / ~~E_{\rm red}/~~V}$ | E <sub>HOMO</sub> /<br>eV | E <sub>LUMO</sub> /<br>eV | $rac{E_{ m g}^{ m ec}}{ m eV}$ | E <sub>HOMO</sub> /<br>eV | E <sub>LUMO</sub> /<br>eV | $E_{ m g}/{ m eV}$ | $\theta_l/^{\mathbf{o}}$ | $	heta_2/^{\mathbf{o}}$ |
| AZ6   | 475(31200)   | 472(54900)  | 0.2             | -1.06                                | -4.93                     | -3.66                     | 1.27                            | -5.26                     | -2.97                     | 2.29               | 25.36                    | 15.01                   |
| AZ261 | 466(21100)   | 464(52200)  | 0.2             | 3 -1.08                              | -4.95                     | -3.64                     | 1.31                            | -5.12                     | -2.67                     | 2.45               | 19.31                    | 20.33                   |
| AZ362 | 488(37800)   | 483(56400)  | 0.2             | 3 -0.97                              | -4.95                     | -3.75                     | 1.20                            | -5.24                     | -3.02                     | 2.22               | 39.50                    | 31.25                   |
| AZ463 | 504(39800)   | 511(56800)  | 0.2             | 2 -0.98                              | -4.94                     | -3.74                     | 1.20                            | -5.17                     | -2.94                     | 2.23               | 9.33                     | 5.96                    |
| AZ564 | 419(31200)   | 449(55300)  | 0.2             | -0.95                                | -4.93                     | -3.77                     | 1.16                            | -5.27                     | -3.11                     | 2.16               | 35.18                    | 25.58                   |

<sup>*a*</sup> Measured in MeCN-DCM (1:1, v/v) solution. <sup>*b*</sup> Measured on 6.5  $\mu$ m TiO<sub>2</sub> films.

<sup>c</sup> Measured by cyclic voltammetry (CV) in MeCN-DCM (3:1, v/v) solution.

<sup>d</sup> Calculated by density functional theory (DFT) with the Gaussian 03 program package at the

B3LYP/6-311G (d, p) level.

# Table 2

| Dye   | $J_{\rm sc}/{ m mAcm}^{-2}$ | $V_{\rm oc}/{ m mV}$ | FF   | PCE/% | IPCE/% ( $\lambda_{max}/nm$ ) |
|-------|-----------------------------|----------------------|------|-------|-------------------------------|
| AZ6   | 15.57                       | 709.0                | 0.65 | 7.18  | 79.65 (490)                   |
| AZ261 | 15.93                       | 720.1                | 0.65 | 7.46  | 81.76 (480)                   |
| AZ362 | 16.63                       | 668.6                | 0.66 | 7.38  | 85.33 (500)                   |
| AZ463 | 16.36                       | 710.0                | 0.66 | 7.68  | 80.56 (510)                   |
| AZ564 | 12.76                       | 729.2                | 0.67 | 6.25  | 73.26 (460)                   |

Photovoltaic performance for DSSCs based on the dyes.

#### **Figure captions**

Fig. 1. Chemical structures of the dyes. Herein  $C_6H_{13}$  denotes *n*-hexyl.

Fig. 2. Synthetic routes of AZ362, AZ463, and AZ564. *Reaction conditions*: (a)  $K_2CO_3$  aqueous solution, Pd(PPh\_3)\_4, TBAB, DMF, 75 °C, 2 h; (b) cyanoacetic acid, CH\_3COONH\_4, CH\_3COOH, reflux, 5 h.

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**Fig. 7.** Dihedral angles of the dyes'  $\pi$ -linker by DFT calculations.

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# Highlights

- A series of cyclic thiourea functionalized dyes containing binary π-linkers were synthesized for DSSCs.
- Increase of short-circuit current by introducing electron-rich segments and broadening absorption band.
- Increase of open-circuit voltage by increasing steric hindrance.
- Binary π-linker bearing 3,4-ethylenedioxythiophene-thiophene shows both large steric hindrance and good conjugated coplanarity.

Supporting Information

Cyclic thiourea functionalized dyes with binary  $\pi$ -linkers: Influence of different  $\pi$ -conjugation segments on the performance of dye-sensitized solar cells

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#### Contents

- 1. Fig. S1 Synthetic routes of 2a, 2b, and 2c.
- 2. Synthetic procedures of 2a, 2b, and 2c.



**Fig. S1** Synthetic routes of **2a**, **2b**, and **2c**. *Reaction conditions*: (i) NBS, THF, 10 °C, 8 h; (ii) 5-formyl-2-thiopheneboronic acid, Na<sub>2</sub>CO<sub>3</sub> aqueous solution, Pd(PPh<sub>3</sub>)<sub>4</sub>, TBAB, THF, 70 °C, 3 h.

2. Synthetic procedures of 2a, 2b, and 2c.

#### 2.1. 2,5-dibromothieno[3,2-b]thiophene (4).

In a 150 mL 3-necked flask, a solution of thienothiophene (TT) (11.2 g, 80 mmol) in dry THF (100 mL) was cooled to 10 °C under a nitrogen atmosphere. NBS (35.6 g, 200 mmol) was added slowly in portions and allowed to stir for 8 h at approximately 10 °C. The reaction mixture was then poured into dichloromethane (DCM). The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the crude product was recrystallized from petroleum ether (PE, boiling range: 60-90 °C) to give a colorless solid (16.2 g, 68% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.14 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 138.31, 121.75, 113.64. GC-MS (EI, *m/z*) calcd for (C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>S<sub>2</sub>): 297.79, found: 297.77.

2.2. 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (5).

1.

The synthesis method resembles that of compound **4** but 3,4-ethylenedioxythiophene (EDOT) instead of TT. Compound **5** was obtained as a colorless solid (17.7 g, 74% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 4.26 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 139.71, 85.54, 64.96. GC-MS (EI, *m/z*) calcd for (C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>2</sub>S): 299.83, found: 299.83.

2.3. 5-(5-bromothieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde (2a).

In a 150 mL 3-necked flask, compound **4** (8.9 g, 30 mmol), 5-formyl-2thiopheneboronic acid (4.7 g, 30 mmol), tetra-*n*-butylammonium bromide (TBAB) (2.9 g, 9 mmol), tetrahydrofuran (THF) (100 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (350 mg, 0.3 mmol) were added in turn under a nitrogen atmosphere. Following this, Na<sub>2</sub>CO<sub>3</sub> aqueous solution (3 mol/L, 20 mL) was added dropwise and the reaction mixture was stirred for 3 h at 70 °C. The reaction mixture was then poured into DCM. The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the crude product obtained was purified by column chromatography (PE/DCM mixture as the eluent) to give a yellow solid (6.7 g, 69% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.86 (s, 1H), 7.67 (d, *J* = 3.6 Hz, 1H), 7.42 (s, 1H), 7.26-7.24 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.31, 146.76, 142.22, 140.18, 138.66, 137.09, 137.00, 124.45, 122.20, 117.67, 115.51. GC-MS (EI, *m*/z) calcd for (C<sub>11</sub>H<sub>5</sub>BrOS<sub>3</sub>): 327.87, found: 327.91.

# 2.4. 5-(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophene-2carbaldehyde (**2b**).

The synthesis method resembles that of compound **2a** but **5** instead of **4**, and the crude product obtained was purified by column chromatography (PE/DCM mixture as the eluent) to give a yellow solid (5.8 g, 59% yield). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 9.88 (s, 1H), 7.95 (d, J = 3.6 Hz, 1H), 7.36 (d, J = 3.2 Hz, 1H), 4.48-4.46 (m,

2H), 4.39-4.37 (m, 2H). GC-MS (EI, *m*/*z*) calcd for (C<sub>11</sub>H<sub>7</sub>BrO<sub>3</sub>S<sub>2</sub>): 331.90, found: 331.90.

#### 2.5. 5-(4-bromophenyl)thiophene-2-carbaldehyde (2c)

The synthesis method resembles that of compound **2a** but 1-bromo-4-iodobenzene instead of **4**, and the crude product obtained was purified by column chromatography (PE/DCM mixture as the eluent) to give a yellow solid (4.4 g, 55% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.88 (s, 1H), 7.72 (d, *J* = 3.9 Hz, 1H), 7.52 (d, *J* = 3.9 Hz, 4H), 7.37 (d, *J* = 4.2 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 182.68, 152.63, 142.83, 137.32, 132.36, 131.99, 127.81, 124.44, 123.61. GC-MS (EI, *m/z*) calcd for (C<sub>11</sub>H<sub>7</sub>BrOS): 267.94, found: 267.49.