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# The effect of anchoring group number on the performance of dye-sensitized solar cells

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### 1. Introduction

### ABSTRACT

Novel dyes comprising a triphenylamine donor, thiophene conjugated bridge and different numbers of anchor groups (cyanoacrylic acid acceptor) were synthesized and employed as photosensitizers in dyesensitized solar cells. The absorbance of the dyes in solution was red shifted and the first oxidation potential decreased with increasing butoxy group:anchor group ratio. Solar cells based on the dyes exhibited energy conversion efficiencies of 6.7–7.4% at 100 mW cm<sup>-2</sup>. Increasing butoxy group:anchor group ratio resulted in higher open-circuit voltage and higher efficiency.

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Dve-sensitized solar cells (DSC) have received considerable attention as a promising low cost candidate for transferring solar energy into electricity since the first, high-efficiency DSC was reported by Grätzel et al. in 1991 [1-3]. Considerable research effort has attended the design of more efficient dyes as these play a very important role in obtaining high power conversion efficiency  $(\eta)$  [4]. The dyes reported so far include metal (ruthenium) complexes and metal-free dyes. DSCs based on ruthenium dyes achieve a power conversion efficiency of 11.1% measured using an air mass of 1.5 (AM 1.5) [5]. In contrast, dyes have received great attention in recent years in view of the rarity and toxicity of ruthenium as well as the high molar extinction coefficient, low cost and flexibility in terms of molecular tailoring, of metal-free dyes, such as coumarins [6–11], triarylamine derivatives [12-31], indolines [32,33] and others [27,31,34-36]. In general, these dyes are of donor-conjugated bridge-acceptor  $(D-\pi-A)$  architecture; the majority of research has focused on changing the  $\pi$ -conjugated linkers or donors.

Dve anchoring in DSCs is critical in achieving high *n*, and typical anchor groups are carboxylate and phosphonate. However, only a few studies have investigated the influence, on DSC performance. of the nature and number of anchor groups in ruthenium and dye sensitizers. Hara et al. found that a monocarboxylate Ru-phenanthroline complex was less efficient than that obtained using di- or tricarboxylate and concluded that two anchoring carboxylates were necessary for effective binding to a TiO<sub>2</sub> surface [37,38]. Park et al. systematically investigated the effects of the nature (carboxylate vs phosphonate) and number (2, 4, and 6) of anchor groups in Ru-bipyridyl complexes on their binding to a TiO<sub>2</sub> surface and the performance of DSCs [39]. During the preparation of this manuscript, a report on the impact of anchor group number on the performance of DSCs appeared [40]. Yang et al. found that in triphenylamine-based, multiple rhodanine-3-acetic acid electron acceptor dyes, those which contained two anchor groups (rhodanine-3-acetic acid) exhibited superior photovoltaic performance than those with one or three anchor groups, owing to red shifts and broadening of absorbance [40].

This paper concerns the synthesis of three novel dyes comprising a triphenylamine (TPA) donor (with 0, 1, or 2 butoxy groups), thiophene conjugated bridge, and cyanoacrylic acid acceptors (3, 2, or 1). The DSC based on dye **S1** (Fig. 1) with two



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Fig. 1. Molecular structures of the three organic dyes.

butoxy groups and one anchor group gave best performance ( $\eta$ : **S1** > **S2** > **S3**), this differing to Yang's experience [40]. The relationship between the number of anchor and butoxy groups and the photophysical, electrochemical, and photovoltaic properties of the dyes are investigated.

### 2. Experimental section

### 2.1. Materials

Unless otherwise stated, starting materials were used as commercially purchased without further purification. Toluene and THF were distilled from sodium-benzophenone under nitrogen before use, DMF was distilled from CaH<sub>2</sub>. Tris[4-(5-formyl-2-thienyl)phenyl]amine (**3d**) [41] was prepared according to literature procedures.

### 2.2. Measurements

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane as an internal standard. Mass spectra were measured on a GCT-MS micromass spectrometer using the electron impact (EI) mode or on a Bruker Daltonics BIFLEX III MALDI-TOF analyzer using MALDI mode. Elemental analyses were carried out using an FLASH EA1112 elemental analyzer. The UV–vis absorption spectra of the dyes in CHCl<sub>3</sub> and adsorbed on TiO<sub>2</sub> films were recorded on a JASCO V-570 spectrophotometer. Cyclic voltammetry measurements in solution were carried out under nitrogen in a deoxygenated solution of tetra*n*-butylammonium hexafluorophosphate (0.1 mol dm<sup>-3</sup>) in either acetonitrile (**S1**) or THF (**S2**) employing a computer-controlled CHI660C electrochemical workstation. A platinum working electrode, a platinum-wire auxiliary electrode and an Ag wire anodized with AgCl as a pseudo-reference electrode were used. **S3** was coated on the platinum working electrode due to its limited solubility. Ferrocene was used as an internal standard. Cyclic voltammogram measurements in  $TiO_2$  film were carried out using dye-loaded  $TiO_2$  films on FTO glass, platinum-wire and Ag/AgCl as working, counter and reference electrodes, respectively. The supporting electrolyte was 0.1 mol dm<sup>-1</sup> tetra-*n*-butylammonium hexafluorophosphate in acetonitrile.

### 2.3. Synthesis

### 2.3.1. N,N-bis(4-butoxyphenyl)-aniline (1a)

A solution of 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.32 mmol, 177 mg), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.16 mmol, 166 mg) and 1-bromo-4-butoxy-benzene (12 mmol, 2.75 g) in anhydrous toluene (20 cm<sup>3</sup>) was stirred under nitrogen at room temperature for 30 min. Aniline (4 mmol, 372 mg) and t-BuONa (20 mmol, 1.93 g) were added and the ensuing reddish-brown coloured suspension was refluxed under nitrogen for 72 h. The reaction mixture was cooled to room temperature; the solid was filtered off and washed with petroleum ether. The organic phase was washed with water, extracted with petroleum ether and dried over anhydrous MgSO<sub>4</sub>. Chromatographic purification (silica gel, petroleum ether) afforded colorless oil (1.01 g, 65%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): δ 7.13 (t, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 4H), 6.90 (d, J = 7.9 Hz, 2H), 6.83 (m, 5H), 3.93 (t, J = 6.4 Hz, 4H), 1.74 (m, 4H), 1.49 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, acetone $d_6$ ):  $\delta$  156.74, 150.17, 142.10, 130.14, 127.62, 121.80, 121.61, 116.46, 68.78, 32.59, 20.39, 14.74. HRMS (EI): m/z 389.2360 (calcd for C<sub>26</sub>H<sub>31</sub>NO<sub>2</sub>, 389.2355). Anal. Calcd for C<sub>26</sub>H<sub>31</sub>NO<sub>2</sub>: C, 80.17; H, 8.02; N, 3.60. Found: C, 80.17; H, 8.17; N, 3.44%.

### 2.3.2. N,N-bis(4-butoxyphenyl)-N-(4-bromophenyl)-amine (1b)

In a two-neck round-bottom flask were added **1a** (0.5 mmol, 195 mg), NBS (0.5 mmol, 89 mg), and 5 cm<sup>3</sup> carbon tetrachloride. The mixture was deoxygenated with nitrogen for 30 min and then refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered, the solvent was removed using rotary evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 25:1) yielding a colorless oil (227 mg, 97%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.28 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 4H), 6.90 (d, *J* = 8.9 Hz, 4H), 6.74 (d, *J* = 8.9 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 4H), 1.74 (m, 4H), 1.49 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>):  $\delta$  156.88, 149.19, 140.92, 132.46, 127.71, 122.00, 116.23, 112.14, 68.41, 32.10, 19.89, 14.14. HRMS (EI): *m*/*z* 467.1464 (calcd for C<sub>26</sub>H<sub>30</sub>BrNO<sub>2</sub>, 467.1460). Anal. Calcd for C<sub>26</sub>H<sub>30</sub>BrNO<sub>2</sub>: C, 66.67; H, 6.46; N, 2.99. Found: C, 66.97; H, 6.61; N, 2.79%.

### 2.3.3. N,N-bis(4-butoxyphenyl)-N-(4-(2-thienyl)phenyl)amine (**1c**)

To a solution of **1b** (1 mmol, 468 mg) and 2-tri-n-butylstannylthiophene (1.5 mmol, 560 mg) in dry toluene (20 cm<sup>3</sup>) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol, 58 mg) under a nitrogen atmosphere. The mixture was stirred at 110 °C for 24 h. After cooling to room temperature, a 10 cm<sup>3</sup> aqueous solution of KF (5 g) was added and the mixture then stirred for 2.5 h. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with 10% aq HCl solution and saturated aq NaHCO<sub>3</sub>. The organic phase was dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography on silica gel using 3:1 hexane/dichloromethane as the eluent yielding a light yellow solid (313 mg, 66%). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.47 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 5.1 Hz, 1H), 7.29 (d, J = 3.5 Hz, 1H),7.07 (d, J = 8.6 Hz, 4H), 7.06 (s, 1H), 6.91 (d, J = 8.6 Hz, 4H), 6.86  $(d, J = 8.2 \text{ Hz}, 2\text{H}), 3.99 (t, J = 6.4 \text{ Hz}, 4\text{H}), 1.75 (m, 4\text{H}), 1.50 (m, 4\text$ 4H), 0.97 (t, I = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, acetone- $d_6$ ): δ 156.79, 149.34, 145.21, 141.22, 128.92, 127.68, 127.19, 127.16, 124.40, 122.61, 120.86, 116.22, 68.47, 32.17, 19.94, 14.17. HRMS (EI): m/z 471.2235 (calcd for C<sub>30</sub>H<sub>33</sub>NO<sub>2</sub>S, 471.2232). Anal. Calcd for C<sub>30</sub>H<sub>33</sub>NO<sub>2</sub>S: C, 76.40; H, 7.05; N, 2.97. Found: C, 76.05; H, 7.04; N, 2.99%.

### 2.3.4. 5-(4-(Bis(4-butoxy-phenyl)amino)phenyl)thiophene-2-carbaldehyde (**1d**)

POCl<sub>3</sub> (caution: reacts violently with water; incompatible with many metals, alcohols, amines, phenol and bases; 1.66 mmol, 254 mg) was added dropwise to a solution of 1c (0.83 mmol, 390 mg) in anhydrous DMF  $(5 \text{ cm}^3)$  under a nitrogen atmosphere. The solution was stirred at 80 °C overnight. After cooling to room temperature, the resulting dark red suspension was washed with water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography on silica gel using 2:1 hexane/dichloromethane as the eluent yielding a yellow solid (311 mg, 75%). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  9.88 (s, 1H), 7.89 (d, J = 4.0 Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 4.0 Hz, 1H),7.11 (d, J = 8.8 Hz, 4H), 6.94 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 8.7 Hz, 2H), 4.00 (t, J = 6.4 Hz, 4H), 1.75 (m, 4H), 1.50 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, acetone- $d_6$ ):  $\delta$  183.37, 157.46, 155.04, 151.19, 142.09, 140.60, 139.41, 128.48, 128.10, 124.98, 123.70, 119.69, 116.49, 68.65, 32.32, 20.12, 14.37. HRMS (EI): *m*/*z* 499.2185 (calcd for C<sub>31</sub>H<sub>33</sub>NO<sub>3</sub>S, 499.2181). Anal. Calcd for C<sub>31</sub>H<sub>33</sub>NO<sub>3</sub>S: C, 74.52; H, 6.66; N, 2.80. Found: C, 74.29; H, 6.79; N, 2.79%.

### 2.3.5. 3-(5-(4-(Bis(4-butoxyphenyl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (**S1**)

To a mixture of 1d (0.48 mmol, 240 mg), cyanoacetic acid (0.72 mmol, 61.2 mg), and ammonium acetate (0.12 mmol, 9.24 mg) was added acetic acid  $(5 \text{ cm}^3)$ . The mixture was deoxygenated with nitrogen for 30 min and was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was washed with water and extracted with CHCl<sub>3</sub>, and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the residue was purified by column chromatography on silica gel using CHCl<sub>3</sub> as eluent yielding a red solid (205 mg, 75%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  13.61 (s, 1H), 8.43 (s, 1H), 7.96 (d, I = 4.0 Hz, 1H), 7.60 (d, I = 8.6 Hz, 2H), 7.57 (d, J = 4.1 Hz, 1H), 7.09 (d, J = 8.5 Hz, 4H), 6.94 (d, J = 8.6 Hz, 4H), 6.76 (d, J = 8.6 Hz, 2H), 3.95 (t, J = 6.4 Hz, 4H), 1.69 (m, 4H), 1.44 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  163.89, 155.90, 154.02, 149.76, 146.52, 141.80, 138.84, 132.87, 127.42, 127.26, 123.18, 123.03, 117.99, 116.70, 115.51, 96.58, 67.32, 30.79, 18.75, 13.68. MS (MALDI): m/z 566 (M<sup>+</sup>). Anal. Calcd for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S: C, 72.06; H, 6.05; N, 4.94. Found: C, 71.61; H, 6.09; N, 4.87%.

### 2.3.6. 4-Butoxy-triphenylamine (2a)

A solution of dppf (0.4 mmol, 222 mg), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.2 mmol, 207 mg) and 1-bromo-4-butoxybenzene (10 mmol, 2.29 g) in anhydrous toluene  $(30 \text{ cm}^3)$  was stirred under nitrogen at room temperature for 30 min. Diphenylamine (5 mmol, 845 mg) and t-BuONa (25 mmol, 2.4 g) were added and the resulting redbrown suspension was refluxed under nitrogen for 72 h. The reaction mixture was cooled to room temperature, the solid was filtered off and washed with petroleum ether. The organic phase was washed with water, extracted with petroleum ether and dried over anhydrous MgSO<sub>4</sub>. Chromatographic purification (silica, petroleum ether) afforded a white solid (1.32 g, 83%). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.26 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 7.7 Hz, 2H), 7.03 (m, 2H), 6.99 (d, J = 7.8 Hz, 4H), 6.93 (m, 4H), 3.99 (t, J = 6.4 Hz, 2H), 1.75 (m, 2H), 1.50 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>): δ 157.12, 149.30, 141.43, 130.15, 128.41, 123.65, 122.86, 116.40, 68.58, 32.31, 20.09, 14.33. HRMS (EI): m/z 317.1782 (calcd for C<sub>22</sub>H<sub>23</sub>NO, 317.1780). Anal. Calcd for C22H23NO: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.11; H, 7.16; N, 4.16%.

### 2.3.7. N,N-bis(4-bromophenyl)-N-(4-butoxyphenyl)-amine (2b)

In a two-neck round-bottom flask was placed **2a** (4.63 mmol, 1.47 g), NBS (9.26 mmol, 1.65 g), and 50 cm<sup>3</sup> carbon tetrachloride. The mixture was deoxygenated with nitrogen for 30 min and refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered. The solvent was removed with rotary evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 35:1) yielding a white solid (2.15 g, 98%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.39 (d, *J* = 8.4 Hz, 4H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.94 (m, 6H), 4.00 (t, *J* = 6.4 Hz, 2H), 1.75 (m, 2H), 1.50 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>):  $\delta$  157.66, 147.97, 140.15, 133.00, 128.67, 125.09, 116.54, 114.83, 68.49, 32.09, 19.89, 14.11. HRMS (EI): *m*/*z* 474.9963 (calcd for C<sub>22</sub>H<sub>21</sub>Br<sub>2</sub>NO, 474.9969). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>Br<sub>2</sub>NO: C, 55.60; H, 4.45; N, 2.95. Found: C, 55.95; H, 4.57; N, 3.00%.

### 2.3.8. N-(4-butoxyphenyl)-N,N-bis(4-(thiophen-2-yl)phenyl)amine (**2c**)

To a solution of **2b** (2.32 mmol, 1.1 g) and 2-tri-n-butylstannylthiophene (7 mmol, 2.6 g) in dry toluene (30 cm<sup>3</sup>) was added Pd (PPh<sub>3</sub>)<sub>4</sub> (0.15 mmol, 173 mg) under a nitrogen atmosphere. The mixture was stirred at 110 °C for 24 h. After cooling to room temperature, a 10  $\text{cm}^3$  aqueous solution of KF (5 g) was added and stirred for 2.5 h. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed subsequently with a 10% HCl aqueous solution and a saturated NaHCO<sub>3</sub> aqueous solution. The organic phase was dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography on silica gel using 15:1 hexane/dichloromethane as the eluent vielding a vellow solid (715 mg, 64%). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.57 (d, I = 8.4 Hz, 4H), 7.37 (m, 4H), 7.12 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 4.8 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 4H), 6.97 (d, J = 8.5 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.77 (m, 2H), 1.51 (dd, I = 14.8 Hz, 7.4 Hz, 2H), 0.98 (t, I = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.41, 148.14, 144.82, 140.53, 129.07, 129.02, 128.55, 127.39, 124.98, 123.70, 123.23, 116.43, 68.50, 32.14, 19.92, 14.13. HRMS (EI): *m*/*z* 481.1538 (calcd for C<sub>30</sub>H<sub>27</sub>NOS<sub>2</sub>, 481.1534). Anal. Calcd for C<sub>30</sub>H<sub>27</sub>NOS<sub>2</sub>: C, 74.81; H, 5.65; N, 2.91. Found: C, 74.86; H, 5.70; N, 2.91%.

## 2.3.9. N-(4-butoxyphenyl)-N,N-bis[4-(5-formyl-2-thienyl)phenyl]-amine(**2d**)

POCl<sub>3</sub> (4.36 mmol, 669 mg) was added dropwise to a solution of 2c (0.87 mmol, 420 mg) in anhydrous DMF (6 cm<sup>3</sup>) under a nitrogen atmosphere. The solution was stirred at 80 °C overnight. After cooling to room temperature, the resulting dark red suspension was washed with water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography on silica gel using 2:1 hexane/ dichloromethane as the eluent yielding an orange solid (262 mg, 56%). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  9.92 (s, 2H), 7.94 (d, *I* = 4.0 Hz, 2H), 7.72 (d, *I* = 8.7 Hz, 4H), 7.57 (d, *I* = 4.0 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 4H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.78 (m, 2H), 1.52 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>): δ 183.53, 158.05, 154.02, 149.38, 142.73, 139.68, 139.23, 129.21, 128.18, 127.64, 124.52, 123.53, 116.63, 68.54, 32.10, 19.91, 14.12. HRMS (EI): m/z 537.1437 (calcd for C<sub>32</sub>H<sub>27</sub>NO<sub>3</sub>S<sub>2</sub>, 537.1432). Anal. Calcd for C<sub>32</sub>H<sub>27</sub>NO<sub>3</sub>S<sub>2</sub>: C, 71.48; H, 5.06; N, 2.60. Found: C, 71.55; H, 5.13; N, 2.80%.

### 2.3.10. 3,3'-(5,5'-(4,4'-(4-Butoxyphenylazanediyl)bis(4,1-

phenylene))bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (S2) To a mixture of 2d (0.37 mmol, 200 mg), cyanoacetic acid (1.48 mmol, 125.8 mg), and ammonium acetate (0.37 mmol, 28.5 mg) was added acetic acid (5 cm<sup>3</sup>). The mixture was deoxygenated with nitrogen for 30 min and was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was washed with water and extracted with CHCl<sub>3</sub>, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the residue was purified by column chromatography on silica gel using CHCl<sub>3</sub> as eluent yielding a red solid (142 mg, 57%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  13.46 (s, 2H), 8.47 (s, 2H), 8.00 (d, I = 4.0 Hz, 2H), 7.71 (d, J = 8.7 Hz, 4H), 7.67 (d, J = 4.0 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H),7.07 (d, *J* = 8.6 Hz, 4H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.71 (m, 2H), 1.45 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 171.95, 163.70, 152.90, 147.93, 146.43, 141.51, 133.71, 128.18, 127.46, 126.04, 124.16, 122.46, 116.61, 115.83, 97.63, 67.39, 30.77,18.74, 13.68. MS (MALDI): *m*/*z* 671 (M<sup>+</sup>). Anal. Calcd for C<sub>38</sub>H<sub>29</sub>N<sub>3</sub>O<sub>5</sub>S<sub>2</sub>: C, 67.94; H, 4.35; N, 6.26. Found: C, 67.69; H, 4.34; N, 6.05%.

## 2.3.11. 3,3',3"-(5,5',5"-(4,4',4"-Nitrilotris(benzene-4,1-diyl))tris (thiophene-5,2-diyl))tris(2-cyanoacrylic acid) (**S3**)

To a mixture of **3d** (0.15 mmol, 86.4 mg), cyanoacetic acid (0.68 mmol, 57.4 mg), and ammonium acetate (0.11 mmol, 8.5 mg) was added acetic acid (3 cm<sup>3</sup>). The mixture was deoxygenated with nitrogen for 30 min and stirred at 120 °C for 40 h. After cooling to room temperature, the mixture was washed with  $CH_2Cl_2$  and then

Soxhlet extracted with CHCl<sub>3</sub> for 65 h to afford a red solid (80 mg, 69%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  13.75 (s, 3H), 8.47 (s, 3H), 8.01 (d, *J* = 4.0 Hz, 3H), 7.78 (d, *J* = 8.5 Hz, 6H), 7.72 (d, *J* = 5.6 Hz, 3H), 7.21 (d, *J* = 8.5 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.69, 151.96, 147.01, 145.83, 140.94, 134.33, 127.68, 124.57, 116.86, 99.15. MS (MALDI): *m*/*z* 776 (M<sup>+</sup>). Anal. Calcd for C<sub>42</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub>: C, 64.93; H, 3.11; N, 7.21. Found: C, 63.88; H, 2.94; N, 7.48%.

### 2.4. Dye adsorption measurements

After the preparation of the  $\text{TiO}_2$  films (as depicted in the following device fabrication section), dye adsorption on  $\text{TiO}_2$  of surface area 4 cm<sup>2</sup> was carried out by immersing the films for 8 h in 20 mL of 0.1 mmol dm<sup>-3</sup> solutions of **S1–3** in dry THF. The difference between the absorbance values of the solution before and after adsorption, as well as the molar extinction coefficient and the volume of the solutions were used to determine the amount of dye molecules adsorbed on the TiO<sub>2</sub> film.

### 2.5. DSC device fabrication and measurements

Two layers of TiO<sub>2</sub> films, main layer and scattering layer, were prepared by doctor blading two different TiO<sub>2</sub> pastes on FTO glass substrate (10  $\Omega$   $\Box^{-1}$ , Nippon Sheet Glass). The first nano-porous layer (TiO<sub>2</sub> particle size: 20 nm, PST-18NR, Catalysts & Chemicals Industries Co., Ltd., Japan) was transparent with thickness of 8 µm, and the second layer (thickness: 4 µm, TiO<sub>2</sub> particle size, 400 nm, from CCI in Japan) was used for increasing the device light harvesting in the red region of the solar emission spectrum. The first layer of TiO<sub>2</sub> was heated at 450 °C for 30 min, and the second layer was heated at 500 °C for 20 min. The resulting film was further treated with 0.04 mol dm<sup>-3</sup> TiCl<sub>4</sub> aqueous solution, and then sintered again at 500 °C for 20 min. After cooling to about 80 °C, the films were immersed into the dye solutions (0.3 mmol dm<sup>-3</sup> S1–3 and N719 in dry ethanol) for 8 h 1 mmol dm<sup>-3</sup> 3 $\alpha$ , 12 $\alpha$ -dihydroxy- $5\beta$ -cholanic acid (DCA) was added to the dye solutions to prevent the dye aggregation on the TiO<sub>2</sub> film. In our experiment, open cells were fabricated in air by clamping the different dyed electrode with Pt-sputtered FTO glass as counter electrode. The electrolyte used here composed of 0.6 mol dm<sup>-3</sup> 1-propyl-3-methylimidazolium iodide, 0.1 mol dm<sup>-3</sup> LiI, 0.05 mol dm<sup>-3</sup> I<sub>2</sub>, and 0.5 mol dm<sup>-3</sup> tert-butylpyridine in the mixture of acetonitrile and valeronitrile (1:1, v/v). All the cells were prepared with active area of 0.2 cm<sup>2</sup>. The action spectra of monochromatic incident photo-to-current conversion efficiency (IPCE) for solar cells were performed using a commercial setup for IPCE measurement (PV-25 DYE, JASCO), and IPCE is defined by IPCE( $\lambda$ ) =  $hcJ_{sc}/e\varphi\lambda$ , where *h* is Planck's constant, *c* is the speed of light in a vacuum, *e* is the electronic charge,  $\lambda$  is the wavelength (m),  $J_{sc}$  is the short-circuit photocurrent density (A m<sup>-2</sup>), and  $\varphi$  is the incident radiation flux (W m<sup>-2</sup>). The photocurrent-voltage (I–V) characteristics were recorded using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination (100 mW  $cm^{-2}$ , Oriel, 67 005).

### 3. Results and discussion

#### 3.1. Synthesis

The synthetic routes of the new dyes S1-3 are illustrated in Scheme 1. All the dyes have been synthesized starting with TPA (with 0–2 butoxy groups) via four routine reactions, including bromination (1b and 2b), Stille coupling (1c and 2c), Vilsmeier formylation (1d and 2d), and Knovenagel condensation reaction (S1–3).





### 3.2. Absorption spectra

The normalized absorption spectra of dyes **S1–3** in dilute chloroform solutions are shown in Fig. 2a. All absorption spectra exhibit a weak absorption band at ca. 350 nm and a strong absorption band at ca. 500 nm. The strong visible absorption peaks are attributed to the intramolecular charge transfer (ICT) transition between the TPA-based donor and the cyanoacrylic acid acceptor [14,15,40]. It is interesting that the main absorption band red shifts and accordingly the optical band gap estimated from the onset

absorption edge ( $E_g$ , Table 1) decreases with decreasing the cyanoacrylic acid anchoring groups and increasing the electrondonating butoxy groups. The increase in electron donating butoxy groups on TPA is beneficial to ICT, resulting in red shift of the main absorption peak. This phenomenon is in sharp contrast to that reported for TPA-based rhodanine-3-acetic acid electron acceptor dyes, in which the main absorption band red shifts with increasing number of the rhodanine-3-acetic acid anchoring groups [40]. On the other hand, the molar extinction coefficient of the dyes increases in order of S1 < S2 < S3 with increasing the number of



Fig. 2. The absorption spectra of S1-3 in CHCl<sub>3</sub> (a) and adsorbed on TiO<sub>2</sub> films (b).

#### Table 1

Absorption and electrochemical properties of the dyes.

Dye	Absorption			Electrochemistry		
	$\frac{\varepsilon_{\max}^{a}}{(10^{4} \text{ mol}^{-1} \text{ dm}^{3} \text{ cm}^{-1})}$	λ <sub>max</sub> b (nm)	λ <sub>max</sub> c (nm)	$E_{g}^{d}$ (eV)	E <sub>ox</sub> e (V)	E <sub>red</sub> <sup>f</sup> (V)
S1	3.3	510	448	2.08	0.93	-1.15
S2	4.6	506	463	2.12	1.08	-1.04
<b>S</b> 3	8.4	484	460	2.24	1.13	-1.11

<sup>a</sup> The molar extinction coefficient at  $\lambda_{max}$  in solution.

<sup>b</sup> Absorption maxima in solution.

<sup>c</sup> Absorption maxima adsorbed on TiO<sub>2</sub> photoelectrode.

<sup>d</sup> Optical bandgap estimated from the absorption edge in solution.

 $^{\rm e}$  The first oxidation potential vs. NHE. Potentials measured vs Fc<sup>+</sup>/Fc were converted to normal hydrogen electrode (NHE) by addition of +0.63 V.

<sup>f</sup> The reduction potential vs. NHE calculated from  $E_{ox} - E_{g}$ .

anchoring groups (Table 1), due to large oscillator strength of the charge transfer transition according to Franck-Condon principle [42]. Fig. 2b shows the absorption spectra of the dyes adsorbed on TiO<sub>2</sub> films. The absorption spectra of **S1–3** blue shift 62, 43, and 24 nm, respectively, compared to that in solution. The blue shift is possibly attributed to the deprotonation of carboxylic acid in the dye molecule upon adsorption on the TiO<sub>2</sub> film [43,44]. However, in TPA-based rhodanine-3-acetic acid electron acceptor dyes, when adsorbed on the TiO<sub>2</sub> surface, the absorption spectra generally red shift relative to that in solution except that with 3 anchoring groups [40]. The main absorption band of **S2** and **S3** red shifts compared to that of **S1**, different from the profile in solution.

### 3.3. Electrochemistry

The electrochemical characteristics of the dyes were investigated by cyclic voltammetry (CV) method in solution and in TiO<sub>2</sub> films. As shown in Fig. 3a, all the dyes show the first oxidation peaks at about 0.9-1.1 V vs NHE attributed to the oxidation of the TPA groups. The first oxidation potential  $E_{ox}$  (vs NHE) of the dyes increases gradually in order of S1 (0.93 V) < S2 (1.08 V) < S3 (1.13 V), and the similar profile was found when they were measured on dye-loaded TiO<sub>2</sub> films (Fig. 3b); the dyes are easier to oxidize with increasing the electron-donating butoxy groups and decreasing the cyanoacrylic acid anchoring groups. All the  $E_{ox}$ values are more positive than the  $I^-/I_3^-$  redox couple (~0.4 V vs NHE), suggesting that there is enough driving force for the dye regeneration reaction to compete efficiently with the recapture of the injected electrons by the dye cation radical. The reduction potential  $E_{\rm red}$  (vs NHE) of the dyes is estimated from the  $E_{\rm ox}$  and  $E_{\rm g}$ . The  $E_{\text{red}}$  values of **S1–3** (-1.15, -1.04 and -1.11 V, respectively) are less sensitive to changing the number of the electron-donating butoxy groups and cyanoacrylic acid anchoring groups. All the Ered values are more negative than the conduction band edge energy level of the TiO<sub>2</sub> electrode, -0.5 V vs NHE [7], indicating that the electron injection process is energetically favorable.

### 3.4. Photovoltaic performance

Action spectrum, incident photon-to-electron conversion efficiency (IPCE) as a function of wavelength, was measured to



**Fig. 3.** Cyclic voltammograms of the dyes (**S1** in CH<sub>3</sub>CN, **S2** in THF and **S3** in film) with ferrocenium/ferrocene as an internal standard (a) and of dye-loaded TiO<sub>2</sub> film on FTO glass (b), at 50 mV s<sup>-1</sup>. The horizontal scale refers to an anodized Ag wire pseudo-reference electrode.



Fig. 4. Photocurrent action spectra of DSCs based on S1-3 with DCA.

evaluate the photoresponse of photoelectrode in the whole spectral region. Fig. 4 shows the IPCE spectra of DSCs based on **S1–3** in the presence of DCA. All three dyes can efficiently convert visible light to photocurrent in the range of 400–700 nm. In the range of 400–500 nm, IPCE maxima of up to 84%, 82% and 83% were achieved for **S1**, **S2** and **S3**, respectively, while the maximum at 535 nm was 84% for the standard N719 based DSC under similar conditions, indicating that efficient photon-to-electron conversion efficiencies for **S1–3** based DSCs. **S2** and **S3** gave broader spectra and higher photoresponse in the long wavelength region (>500 nm) than **S1**, which was consistent with the corresponding absorption spectra on transparent TiO<sub>2</sub> film. It should be noted that **S1–3** based DSCs gave higher IPCE values in 400–500 nm region as compared with N719 based device.

According to the photocurrent action spectra, one may expect higher short-circuit photocurrent densities ( $J_{sc}$ ) for **S2**- and **S3**-based DSCs from the overlap integral of IPCE curves with the standard AM 1.5 solar emission spectrum. Indeed, both **S2**- and **S3**-based DSCs give higher  $J_{sc}$  (16.95 and 17.30 mA cm<sup>-2</sup>) than **S1**-based DSC (16.59 mA cm<sup>-2</sup>, see Fig. 5 and Table 2), which is consistent with the IPCE data. The sensitizer with more cyanoacrylic acid



Fig. 5. Current density-voltage curves of DSCs sensitized with S1-3 and N719 with DCA under simulated AM 1.5, 100 mW cm<sup>-2</sup>.

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Photovoltaic performances of DSCs based on S1-3 and N719 without and with DCA.

	dye	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	$V_{\rm oc}({\rm mV})$	ff	η (%)	Amount <sup>a</sup> $(10^{-7} \text{ mol cm}^{-2})$
Without DCA	S1	16.80	630	0.63	6.65	2.29
	S2	16.53	570	0.58	5.49	1.76
	<b>S</b> 3	16.77	565	0.53	5.34	2.42
With DCA	<b>S1</b>	16.59	685	0.65	7.38	
	S2	16.95	635	0.66	7.10	
	<b>S3</b>	17.30	620	0.63	6.75	
	N719	18.87	675	0.64	8.15	

<sup>a</sup> Amount of dye adsorbed on TiO<sub>2</sub> film.

anchoring groups upon adsorption transfers more protons to the  $TiO_2$  surface, leading to the positive shift of the conduction band edge of  $TiO_2$ . Thus, the sensitizer with more anchoring groups possesses larger gap between its LUMO and the conduction band level of the  $TiO_2$ , leading to more efficient electron injection into  $TiO_2$  photoelectrode and thus to increase in the short-circuit photocurrent density.

The values of fill factor (*ff*) are almost the same, but open-circuit voltages ( $V_{oc}$ ) decreased in order of **S1** > **S2** > **S3**. The decrease of  $V_{oc}$  is generally associated with the positive shift of conduction band edge of TiO<sub>2</sub> photoanode [45] and/or enhancement of charge recombination at the TiO<sub>2</sub>/dye/electrolyte interface [42]. The sensitizer with more anchoring groups upon adsorption transfers more protons to the TiO<sub>2</sub> surface, charging it more positively, leading to lower conduction band of TiO<sub>2</sub> and lower  $V_{oc}$ . On the other hand, decreasing the electron-donating butoxy groups and increasing the cyanoacrylic acid anchoring groups could lead to increased charge recombination and lower  $V_{oc}$ . The good suppression function to the charge recombination of alkoxy chains has also been reported by Wang et al. [42].

Although the DSC sensitized with **S1** exhibits the lowest  $J_{sc}$  (16.59 mA cm<sup>-2</sup>) and a moderate ff(0.65), the highest  $V_{oc}$  (685 mV) leads to the highest  $\eta$  (7.38%). In the same geometry DSC, the widely used dye N719 gave  $V_{oc}$  of 675 mV, ff of 0.64,  $J_{sc}$  of 18.87 mA cm<sup>-2</sup>, and  $\eta$  of 8.15%.  $\eta$  decreased in order of **S1** > **S2** > **S3**. Clearly, the efficiencies of the DSCs are susceptible to changing the number of anchoring groups/butoxy groups in the dyes. The more anchoring groups the dye has, the lower efficiency the device exhibits. Our result is different from Yang's example, in which the dye with two anchoring groups exhibited the best efficiency [40].

We also investigated the performances of the **S1–3** based devices without DCA (see Table 2). The values of  $J_{sc}$ ,  $V_{oc}$ , ff and  $\eta$  without DCA dominantly decreased compared to those with DCA, probably due to dye aggregation. The amount of dyes adsorbed on TiO<sub>2</sub> film without addition of DCA was measured (Table 2). The adsorption amount of **S2** was lower than that of **S1** and **S3**, possibly responsible for its lower  $J_{sc}$ .

### 4. Conclusion

We have synthesized three new organic sensitizers composed of different numbers of anchoring groups/butoxy groups for dyesensitized solar cells and obtained some insight into their structure–property relationships. The absorption spectrum in solution red shifts, the absorption spectrum adsorbed on TiO<sub>2</sub> films blue shifts, and the first oxidation potential decreases with increasing butoxy groups/decreasing anchoring groups. Two butoxy groups on the TPA donor of **S1** (with one anchoring group) can suppress charge recombination and increase  $V_{oc}$  and *ff* of DSCs, giving the highest  $\eta$  of 7.38%, 90% of that for N719-based device fabricated under similar conditions. The DSC based on **S3** with three cyanoacrylic acid anchoring groups shows the lowest  $\eta$ . The number of anchoring groups/butoxy groups exerts a significant impact on  $V_{oc}$ ,  $J_{sc}$  and  $\eta$ . Increasing anchoring group/butoxy group ratio leads to lower  $V_{oc}$ , due to the positive shift of conduction band edge of TiO<sub>2</sub> and more charge recombination, higher  $J_{sc}$  and finally to lower efficiency. Therefore, our work may give a useful guidance for the molecular design of the organic dyes used in dye-sensitized solar cells.

### **Disclosure statement**

The authors declare no conflict of interest.

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