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# Structure–property relationship of different electron donors: novel organic sensitizers based on fused dithienothiophene $\pi$ -conjugated linker for high efficiency dye-sensitized solar cells



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#### 1. Introduction

Compared to Ru(II)-based sensitizers, organic dyes have recently received considerable academic and industrial attention owing to the wide spectrum of possible chromophores that can be used, high molar extinction coefficient, ease of structure modifications, tunable ground and excited states oxidation potentials, and low cost of materials and fabrications.<sup>1–16</sup> The most common building block of organic dyes designed for DSCs comprises an electron donor, a  $\pi$ -conjugated spacer, and an electron acceptor, typically cyanoacrylic acid. For high efficiency DSCs, dyes should be molecularly designed to harvest photons with high molar absorptivity across a wide bandwidth of the solar spectrum covering the

#### ABSTRACT

Three novel organic dyes, coded **Ba-01–03**, based on  $D-\pi$ –A building blocks were synthesized and characterized for dye-sensitized solar cells (DSCs) to study the influence of different electron donors on photocurrent and photovoltage. The electron donor of **Ba-01** was based on *N*-methoxyphenylcarbazole and the electron donors for **Ba-02** and **Ba-03** were based on different indoline analogs. The photovoltaic performance of these sensitizers was characterized using incident-photon-to-current conversion efficiency (IPCE), photovoltage measurements, and total solar-to-electric conversion efficiency ( $\eta$ ). It was shown that photovoltage of indoline donor based dye **Ba-03** showed the highest efficiency of 6.38% compared to carbazole donor based dye of **Ba-01**. DFT calculations were proven to be an effective tool in the prediction of the vertical electronic excitation, charge separation, and photovoltage as it effectively predicted the delocalization and coefficient size of the HOMO and LUMO for **Ba-01–03**.

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visible including the red region and extended up to the NIR region while the ground and excited states oxidation potentials of the dyes should be maintained thermodynamically favorable for the reduction of the oxidized dye with the electrolyte and electron injection from the excited state of the dye into the conduction band (CB) edge of TiO<sub>2</sub>, respectively. Recently, Ru-based black dye showed remarkable efficiency of 11.4%, which has  $E_{0-0}$  energy gap of 1.6 eV.<sup>16</sup> However, most of the efficient organic dyes have an  $E_{0-0}$ energy gap of >2.0 eV. Therefore, there is still much room to tune the HOMO–LUMO energy level to enhance light harvesting ability, to achieve a high extinction coefficient, and to shift the energy levels to improve the performance of the solar cell. To achieve this we have selected here fused thiophene as  $\pi$ -linker as it has been exhibited strong electron injection properties into thin film.<sup>17,18</sup> Furthermore, this fused ring system has been used to design new organic sensitizers to get higher light harvesting and high total conversion efficiency of DSCs.<sup>19–21</sup> Recently, it was also reported that employing a nonlinear structure and long aliphatic chain prevents dye aggregation and minimize charge re-combinations,

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respectively.<sup>22</sup> Molecular modeling investigation using DFT/TD-DFT can also be a valuable screening tool, where it can be used effectively prior to synthesis to screen several hundreds of dyes to identify the most promising candidates that meet the above requirements of efficient sensitizers for DSCs.

In this work, we present herewith a study that combines experimental and DFT/TD-DFT molecular modeling of a novel series of low molecular weight organic sensitizers based on fused dithienothiophene (Ba-01-03) for DSCs (Fig. 1) to study the different electron donors on the photovoltaic performance of these sensitizers. While **Ba-01** is based on carbazole electron donor, sp<sup>2</sup>carbons, Ba-02 and Ba-03 are based on different indoline electron donor analogy, comprised of some sp<sup>3</sup> carbons. Previously, we reported that organic sensitizers containing the strong indoline donor showed strong and intense absorption bands in the visible region.<sup>23</sup> In addition, this unit has a tendency to prevent  $\pi$ -stacked aggregation on the semiconductor surface. To enhance our understanding for developing high performances organic sensitizers, we selected here another effective well known carbazole donor to investigate the DSCs performances.<sup>24</sup> It was expected that the indoline-based electron donor would furnish sensitizers for DSCs that would exhibit much higher efficiency  $(\eta)$ , compared to carbazole-based donor sensitizers.



Fig. 1. Molecular structures of Ba-01-03.

#### 2. Results and discussion

### 2.1. Synthesis

New dyes **Ba-01–03** were synthesized in a straightforward manner, and they were obtained in a range of 47–50% yields from their precursors **4**, **7**, and **10** (Schemes 1–3, and see Experimental section).

#### 2.2. Molecular modeling

Ground state equilibrium molecular geometries of **Ba-01–03** were calculated using the hybrid DFT energy functional B3LYP<sup>25,26</sup> and the basis set DGDZVP (density Gauss double-ζ with polarization functions).<sup>27,28</sup> Subsequently, a single point energy calculation was performed on the optimized geometry using different long-range corrected time-dependent DFT energy functional methods including CAM-B3LYP<sup>29</sup> with the basis set DGDZVP, and the electronic absorption spectra were extracted. The TD-DFT calculations were performed in ethanol using the polarizable conductor calculation model (PCM). The DFT/TD-DFT calculations were performed on the East Carolina University's Super Computer Jasta using 8 processors and 4 GB of RAM. The solvent effect was accounted for using the polarizable conductor calculation model (PCM), implemented in Gaussian 09. All calculations were performed using Gaussian 09.

#### 2.3. Fabrication of dye-sensitized solar cells

A double-layer TiO<sub>2</sub> photoelectrode,  $(10+5) \mu m$  in thickness with a 10  $\mu$ m thick nanoporous layer and a 5  $\mu$ m thick scattering layer (area: 0.25 cm<sup>2</sup>), was prepared by screen printing on conducting glass substrate. A dve solution of  $3 \times 10^{-4}$  M concentration in acetonitrile/*tert*-butyl alcohol (1/1, v/v) was used to up-take the dve on to the TiO<sub>2</sub> film. Deoxycholic acid (DCA) (20 mM) as a coadsorbent was added into the dye solution to prevent aggregation of the dye molecules. The TiO<sub>2</sub> films were immersed into the dye solution and then kept at 25 °C for 30 h. Photovoltaic measurements were performed in a sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I<sub>2</sub>, 0.1 M LiI, and 0.5 M tert-butylpyridine (TBP) in acetonitrile (AN). The dyedeposited TiO<sub>2</sub> film and a platinum-coated conducting glass were separated by a Surlyn spacer (40 µm thick) and sealed by heating the polymer frame. Photocurrent density-voltage (I-V) of sealed solar cells was measured under AM 1.5G simulated solar light at a light intensity of 100 mW cm<sup>-2</sup> with a metal mask of 0.25 cm<sup>2</sup>. The photovoltaic parameters, i.e., short circuit current  $(J_{sc})$ , open circuit voltage ( $V_{oc}$ ), fill factor (*ff*), and power conversion efficiency  $(\eta)$  were estimated from *I*–*V* characteristics under illumination.

#### 2.4. Photophysical properties

Fig. 2a shows the experimental absorption spectra of dves **Ba**-01–03 in ethanol. Dves Ba-02 and Ba-03 showed significant red shifted absorption maxima  $(\pi - \pi^*)$  at 481 and 485 nm, respectively. compared to 428 nm of dye Ba-01. The absorption band edge of Ba-02 and Ba-03 was extended to 650 nm compared to 550 nm in the case of Ba-01. On the other hand, the extinction coefficient of Ba-02 and **Ba-03** was significantly higher than dye **Ba-01**. When dyes absorbed on a transparent thin TiO<sub>2</sub> film, all dyes exhibited broad absorption spectra similar to those in solution, due to the interaction between the carboxylate group and TiO<sub>2</sub> (Fig. 2b). Upon adsorption on the TiO<sub>2</sub> film, the tail of the absorption spectrum of Ba-02-03 dyes extended up to 700 nm, which is red-shifted by 50 nm compared to the carbazole donor based dye of Ba-01. This broadening of absorption spectrum is highly desirable for harvesting more of the solar spectrum and translates into greater photocurrent.

The ionization potential (IP) of **Ba-01–03** bound to the nanocrystalline TiO<sub>2</sub> film was measured using the photoemission yield spectrometer (Riken Keiki, AC-3E). Ground-state oxidation potential,  $S^{+/0}$ , values of -5.39 eV, -5.31 eV, and -5.26 eV were obtained for sensitizers Ba-01, Ba-02, and Ba-03, respectively. The IP values of **BA-01–03**, which correspond to  $S^{+/0}$ , were sufficiently lower than the redox potential of  $I/I_3$  (–5.10 eV),<sup>30</sup> which ensured favorable thermodynamic ground states for efficient regeneration of the dye through the reaction of the oxidized dye with iodide. The IP values of the indoline containing sensitizers (Ba-02-03) were shifted to anodic direction, compared to the carbazole-based dye (Ba-01) (Table 1). This anodic shift is due to the higher donating ability of indoline donor, compared to carbazole donor, which furnished more charge transfer from D to A in indoline-based dyes (Ba-02–03) than that of the carbazole-based dye (Ba-01). Moreover, the anodic shift increased the negative free energy of electron injection, which explained why Ba-02-03 furnished more photocurrent than **Ba-01**. The onset of the optical energy gap  $(E_{0-0})$  of **Ba-**01-03 dyes was in the range of 1.86-1.94 eV (Table 1). The excitedstate oxidation potential,  $S^{+/*}$ , of sensitizers **Ba-01–03** was in the range of -3.45 to -3.40 eV (Table 1) and lay above the conduction band edge  $(-4.2 \text{ eV})^{31}$  of the nanocrystalline TiO<sub>2</sub> ensuring that the excited states of these dyes are thermodynamically driven for efficient electron injection into the conduction band edge of TiO<sub>2</sub>.





Scheme 1. Synthesis of new organic dye Ba-01.



Scheme 3. Synthesis of new organic dye Ba-03.

Fig. 3 shows the calculated absorption spectrum in ethanol using TD-DFT with the energy functional CAM-B3LYP and basis set DGDZVP. While excellent agreement between the experimental and calculated absorption maxima in ethanol for **Ba-02** and **Ba-03** (Table 2) were found, the calculated  $\lambda_{max}$  for **Ba-01** was overestimated by 0.27 eV.

Fig. 4 shows the delocalization of the HOMO and LUMO of **Ba-01–03**. HOMOs are delocalized over the entire molecules except COOH. The LUMOs were located on the electron acceptor segment and extended up to the electron donor, confirming efficient charge transfer and absence of charge traps.

#### 2.5. Photovoltaic properties

Fig. 5 shows the *I*–*V* curves and Table 3 shows the photovoltaic parameters for dyes **Ba-01–03**. The sensitizer **Ba-02–03** showed higher power conversion efficiency than **Ba-01**, as shown in Table 3. The higher photocurrent of dye **Ba-02–03** can be attributed to the stronger donating ability of indoline analogs. The dye **Ba-03** showed highest overall conversion efficiency ( $\eta$ ) of 6.38% with *J*<sub>sc</sub> of 16.17 mA cm<sup>-2</sup>, *V*<sub>oc</sub> of 0.595 V, *ff* of 0.663, on the other hand, **Ba-01** showed a *J*<sub>sc</sub> of 13.45 mA cm<sup>-2</sup>, *V*<sub>oc</sub> of 0.618 V and *ff* of 0.679, corresponding to an overall efficiency ( $\eta$ ) of 5.64% under the same



Fig. 2. Absorption spectra of Ba-01-03 in ethanol (left) and on TiO<sub>2</sub> film (right).

Table 1Photophysical properties of dyesBa-01-03

Dye	$\lambda_{max}/nm^a$ ( $\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	λ <sub>onset</sub> /nm <sup>b</sup> on TiO <sub>2</sub> film	(IP) <sup>c</sup> (eV)	$E_{0-0}$ (eV) <sup>d</sup>	S <sup>+/</sup> * <sup>c</sup> (eV) <sup>e</sup>
Ba-01	428 (3.5)	610	-5.39	1.94	-3.45
Ba-02	353, 481 (4.0)	660	-5.31	1.88	-3.43
Ba-03	358, 485 (4.1)	665	-5.26	1.86	-3.40

<sup>a</sup> Absorption maxima, measured in ethanol at room temperature.

<sup>b</sup> Absorption measured on a transparent 4  $\mu$ m TiO<sub>2</sub> film. Adsorbed dye concentration on TiO<sub>2</sub> (mol cm<sup>-2</sup>); **Ba-01**, 2.9×10<sup>-7</sup>; **Ba-02**, 3.3×10<sup>-7</sup>; **Ba-03**, 3.4×10<sup>-7</sup>. <sup>c</sup> Ionization potential (IP) of absorbed dyes on the nanocrystalline TiO<sub>2</sub> film was determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E).

<sup>d</sup>  $E_{0-0}$  was estimated from the absorption onset of dye loaded on TiO<sub>2</sub> film. <sup>e</sup> The excited-state oxidation potential,  $S^{+/_{*}}$  levels were calculated from the ex-

pression of  $S^{+/*}=IP-E_{0-0}$ .



Fig. 3. The calculated absorption spectra in ethanol of **Ba-01–03**.

Table 2 Comparison between the calculated and experimental  $\lambda_{max}$  of dyes Ba-01-03

Dyes	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)		
	Expt.	Calcd		
Ba-01	428	471		
Ba-02	481	483		
Ba-03	485	488		

conditions. The  $V_{oc}$  values of **Ba-02** and **Ba-03** are lower than that of **Ba-01** may be due the higher level of ground state oxidation potential of **Ba-02–03** than **Ba-01**, which enhanced the back electron transfer from conduction band to the oxidized dye.

Fig. 6 shows the monochromatic incident-photon-to-current conversion efficiency (IPCE) for DSCs based on **Ba-01–03**. Dye **Ba-03** showed excellent sensitization of nanocrystalline TiO<sub>2</sub> from 400 to 600 nm with a quantum efficiency of >85% in the plateau region and the sensitization covered a broader range of the solar spectrum with onset at a longer wavelength of 810 nm compared to that **Ba-01** with onset at 720 nm. On the other hand, in the case of **Ba-02**, the sensitization also covered a broader range of the solar spectrum with onset similar to **Ba-03**, but quantum efficiency was about 80% in the plateau region 400–600 nm.

#### 3. Conclusions

A novel series (**Ba-01–03**) of low molecular weight sensitizers based on  $D-\pi-A$  building block of fused thiophene was synthesized and characterized for DSCs with **Ba-03** showing impressive total solar-to-electric conversion efficiency of 6.38%. It has become clear that the indoline-based electron donor is better than the carbazole donor. DFT utilizing the energy functional CAM-B3LYP and DGDZVP basis set was proven to be effective in the prediction of vertical electronic excitation and delocalization of HOMOs and LUMOs, which provided invaluable insights into the charge separation efficiency and photovoltage performance of the sensitizers.

#### 4. Experimental section

#### 4.1. General information for materials synthesis

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on JEOL JMTC-270/ 54/SS (JASTEC, 400 MHz) spectrometers. <sup>1</sup>H NMR spectra are reported as follows: chemical shift in parts per million ( $\delta$ ) relative to the chemical shift of CDCl<sub>3</sub> at 7.26 ppm, integration, multiplicities (s=singlet, d=doublet, t=triplet, q=quartet and m=multiple), and coupling constants (hertz). <sup>13</sup>C NMR spectra reported in ppm ( $\delta$ ) relative to the central line of triplet for CDCl<sub>3</sub> at 77.00 ppm. Highresolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing silica gel 60N (spherical, neutral, 40–100 µm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F<sub>254</sub> (Merck). All other



Fig. 4. Delocalization of HOMO and LUMO on Ba-01-03.

reagents and solvents commercially available were used without further purification unless otherwise noted. The compound **1**, **2**, **5**, and **8** were synthesized according to the literature method.<sup>132</sup>

#### 4.2. Synthesis of compounds 3, 6, 9

4.2.1. Compound **3**. Compound **1** (1 mmol), **2** (1.2 mmol), and tetrakis(triphenylphosphine)palladium (20 mol %, 0.2311 g) were dissolved in the mixture of THF (30 mL) and 2 N potassium carbonate aqueous solution (6 mL). The reaction was performed at 70 °C for 12 h under Ar. Then the mixture was poured into water and extracted three times with  $CH_2Cl_2$ . The organic layer was washed with a sodium carbonate aqueous solution and  $H_2O$ , and subsequently dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto



Fig. 5. Photocurrent voltage characteristics of DSCs sensitized with dyes Ba-01-03.

Table 3Photovoltaic performances of dyesBa-01-03<sup>a</sup>

Dyes	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	$V_{\rm oc}$ [V]	ff	Eff, h [%]
Ba-01	13.45	0.618	0.679	5.64
Ba-02	15.85	0.589	0.671	6.11
Ba-03	16.17	0.595	0.663	6.38

<sup>a</sup> Measurements were performed under AM 1.5 irradiation on the DSC devices with 0.25 cm<sup>2</sup> active surface area defined by a metal mask.  $J_{sc}$ : short circuit current;  $V_{oc}$ : open circuit voltage; ff: fill factor;  $\eta$ : conversion efficiency.



Fig. 6. Photocurrent action spectra (IPCE) obtained with dyes  $Ba\mbox{-}01\mbox{-}03$  anchored on nanocrystalline  $TiO_2$  film.

silica-gel column with toluene/hexane (1:5, v/v) as eluant to get compound **3**. Yield 56%; <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  3.88 (s, 3H), 7.22 (d, *J*=8.5 Hz, 2H), 7.26–7.36 (m, 3H), 7.45 (dd, *J*=7.8 Hz, 7.8 Hz, 1H), 7.53 (d, *J*=6.3 Hz, 3H), 7.70 (d, *J*=5.1 Hz, 1H), 7.77 (d, *J*=8.5 Hz, 1H), 7.96 (s, 1H), 8.33 (d, *J*=7.8 Hz, 1H), 8.60 (s, 1H). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz):  $\delta$  55.4, 109.7, 110.2, 115.2, 116.4, 117.3, 120.0, 120.7, 121.4, 122.1, 123.0, 123.9, 125.8, 126.6, 127.1, 128.0, 128.8, 130.2, 140.2, 140.55, 141.0, 142.0, 145.2, 158.5.

4.2.2. Compound **6**. Following the same procedures of compound **3**, the compound **6** was obtained as shown in Scheme 2. Yield 50%; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  1.35–1.48 (m, 1H), 1.55–1.85 (m, 4H), 1.95–2.10 (m, 1H), 2.28 (s, 3H), 3.86 (dd, *J*=7.8 Hz, 8.0 Hz, 1H), 4.88 (dd, *J*=6.3 Hz, 6.3 Hz, 1H), 6.86 (d, *J*=8.5 Hz, 1H), 7.15–7.25 (m, 4H), 7.33 (dd, 1.7 Hz, 8.1 Hz, 1H), 7.46 (s, 1H), 7.52 (d, *J*=5.1 Hz, 1H),

7.67 (d, *J*=5.4 Hz, 1H), 7.73 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz):  $\delta$  20.4, 24.0, 33.1, 34.8, 44.5, 68.3, 107.0, 114.8, 119.6, 121.3, 121.7, 123.9, 124.9, 126.7, 126.9, 129.7, 130.2, 130.8, 135.6, 139.3, 140.1, 142.0, 145.4, 147.2.

4.2.3. Compound **9**. Following the same procedures of compound **3**, the compound **9** was obtained as shown in Scheme 3. Yield 42%; <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  1.35–1.48 (m, 1H), 1.55–1.85 (m, 4H), 1.95–2.10 (m, 1H), 3.75 (s, 3H), 3.80–3.86 (m, 1H), 4.80–4.86 (m, 1H), 6.66 (d, *J*=8.3 Hz, 1H), 6.97 (d, *J*=9.0 Hz, 2H), 7.21–7.32 (m, 3H), 7.43 (s, 1H), 7.50 (d, *J*=5.1 Hz, 1H), 7.65 (d, *J*=5.1 Hz, 1H), 7.69 (s, 1H). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz):  $\delta$  24.0, 32.9, 35.0, 44.5, 55.2, 68.9, 106.2, 114.5, 114.6, 121.3, 121.7, 122.4, 123.3, 124.9, 126.6, 126.8, 130.2, 134.9, 135.2, 140.1, 142.0, 145.5, 148.3, 154.8.

#### 4.3. Synthesis of compounds 4, 7, 10

4.3.1. Compound **4**. Compound **3** (1 mmol) was dissolved in THF (20 mL). After cooling the solution to  $-78 \,^{\circ}$ C, *n*-BuLi (1.2 equiv) was added drop-wise. The reaction mixture was kept at  $-78 \,^{\circ}$ C for 0.5 h under Ar. Then 10 equiv DMF was added into the reaction mixture and warming to room temperature slowly. The reaction mixture was stirred at room temperature for 1 h, and reaction was quenched by H<sub>2</sub>O, and purified by silica-gel column chromatography to give compound **4** in 62% yields. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  3.88 (s, 3H), 7.23 (d, *J*=9.0 Hz, 2H), 7.29–7.40 (m, 3H), 7.46 (dd, *J*=7.3 Hz, 7.8 Hz, 1H), 7.55 (d, *J*=8.8 Hz, 2H), 7.81 (d, *J*=8.5 Hz, 1H), 8.07 (s, 1H), 8.35 (d, *J*=7.6 Hz, 1H), 8.48 (s, 1H), 8.66 (s, 1H), 9.98 (s, 1H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100 MHz):  $\delta$  55.0, 109.8, 110.2, 115.1, 115.8, 117.6, 120.0, 120.3, 122.9, 123.8, 124.0, 126.0, 126.3, 128.3, 128.6, 129.7, 130.4, 140.5, 141.5, 142.0, 144.0, 147.1, 150.2, 159.5, 182.1.

4.3.2. Compound **7**. Following the same procedures as for compound **4**, the compound **7** was obtained as shown in Scheme 2. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  1.35–1.48 (m, 1H), 1.55–1.85 (m, 4H), 1.95–2.10 (m, 1H), 2.29 (s, 3H), 3.86 (dd, *J*=8.1 Hz, 8.5 Hz, 1H), 4.90 (dd, *J*=5.9 Hz, 7.1 Hz, 1H), 6.86 (d, *J*=8.3 Hz, 1H), 7.15–7.25 (m, 4H), 7.38 (d, *J*=8.5 Hz, 1H), 7.52 (s, 1H), 7.82 (s, 1H), 8.44 (s, 1H), 9.94 (s, 1H).

4.3.3. Compound **10**. Following the same procedures as for compound **4**, the compound **10** was obtained as shown in Scheme 3. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  1.35–1.48 (m, 1H), 1.55–1.85 (m, 4H), 1.95–2.10 (m, 1H), 3.75 (s, 3H), 3.80–3.90 (m, 1H), 4.83–4.88 (m, 1H), 6.65 (d, *J*=8.5 Hz, 1H), 6.97 (d, *J*=9.0 Hz, 2H), 7.22–7.28 (m, 2H), 7.34 (d, *J*=8.1 Hz, 1H), 7.48 (s, 1H), 7.79 (s, 1H), 8.44 (s, 1H), 9.94 (s, 1H). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz):  $\delta$  23.9, 32.9, 35.0, 44.5, 55.2, 68.9, 106.1, 114.6, 114.7, 121.9, 122.6, 122.7, 125.5, 126.5, 132.5, 134.6, 135.3, 140.0, 142.3, 147.4, 149.0, 149.8, 155.0, 183.9.

#### 4.4. Synthesis of dyes Ba-01-03

A mixture of the corresponding aldehyde (1.2 mmol), 2cyanoacetic acid (306 mg, 3.6 mmol), and ammonium acetate (46 mg, 0.6 mmol) was dissolved in 10 mL acetonitrile and 10 mL acetic acid, and the mixture was stirred for 12 h in Ar under reflux condition. After evaporation of the solvent, the residue was purified by silica-gel column chromatography to give compounds **Ba-01–03** in 47–50% yields.

4.4.1. Compound **Ba-01**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 3.88 (s, 3H), 7.22 (d, *J*=9.0 Hz, 2H), 7.28–7.36 (m, 3H), 7.46 (dd, *J*=7.1 Hz, 7.8 Hz, 1H), 7.50–7.55 (m, 2H), 7.77 (d, *J*=8.1 Hz, 1H), 8.02 (s, 1H), 8.09 (s, 1H), 8.17 (s, 1H), 8.34 (d, *J*=7.8 Hz, 1H), 8.63 (s, 1H). HRMS

(ESI): m/z: calcd for  $C_{31}H_{18}N_2O_3S_3$  (M–H), 561.04068; found, 561.04051.

4.4.2. Compound **Ba-02**. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  1.35–1.48 (m, 1H), 1.55–1.85 (m, 4H), 1.95–2.10 (m, 1H), 2.28 (s, 3H), 3.82–3.90 (m, 1H), 4.86–4.95 (m, 1H), 6.86 (d, *J*=8.3 Hz, 1H), 7.15–7.25 (m, 4H), 7.38 (d, *J*=8.3 Hz, 1H), 7.51 (s, 1H), 7.83 (s, 1H), 8.35 (s, 1H), 8.55 (s, 1H). HRMS (ESI): *m/z*: calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub> (M–H), 537.07706; found, 537.07698.

4.4.3. Compound **Ba-03**. <sup>1</sup>H NMR (THF- $d_8$ , 400 MHz):  $\delta$  2.40–3.15 (m, 6H), 4.80 (s, 3H), 4.85–4.92 (m, 1H), 5.86–5.95 (m, 1H), 7.70 (d, *J*=8.3 Hz, 1H), 8.0 (d, *J*=8.8 Hz, 2H), 8.28 (d, *J*=8.5 Hz, 2H), 8.36 (d, *J*=8.3 Hz, 1H), 8.50 (s, 1H), 8.79 (s, 1H), 9.13 (s, 1H), 9.23 (s, 1H). HRMS (ESI): *m/z*: calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S<sub>3</sub> (M–H), 553.07198; found, 553.07192.

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#### Supplementary data

Absorption spectra of **Ba-01–03** in 1,4-dioxane,<sup>33</sup> HRMS (ESI) and H NMR spectra of **Ba-01–03**, <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3**, **6**, and **9** are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.02.058.

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- A referee gave the following comment. Some researchers reported that the 33. blue-shift of absorption maximum in solution is attributed to dissociation of proton from carboxyl group, leading to lowering of its electron-withdrawing ability. Therefore, to gain insight into the optical properties of these three dves, authors should measure the absorption spectra in non-polar solvents. such as 1,4-dioxane. Our response is following: the excited-state oxidation potential,  $S^{+/*}$  levels were calculated from the expression of  $S^{+/*}=IP-E_{0-0}$ , where the  $E_{0-0}$  was estimated from the absorption onset of dye loaded on TiO<sub>2</sub> film as shown in Fig. 2b. It was also observed from Table 1 that the excited-state oxidation potential of all three dyes (Ba-01: -3.45 eV, Ba-02: -3.43 eV, Ba-03: 3.40 eV) lay above the conduction band edge (-4.2 eV) of the nanocrystalline TiO<sub>2</sub> ensuring that the excited states of the dyes are thermodynamically driven for efficient electron injection into the conduction band edge of TiO<sub>2</sub>. Therefore, authors think that the absorption spectra in ethanol is enough for this manuscript. However, according to the comment of the referee, the spectra in 1,4-dioxane were measured and shown in ESI.