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# Effect of Anchoring Group in Anthracene/ Thiophene-Bridged Triphenylamine-Based Organic Dyes for Dye-Sensitized Solar Cells

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Triphenylamine-based metal-free organic dyes (D1–D3) with different electron acceptors such as 2-cyanoacetic acid, rhodanine-3-acetic acid, or 5-oxo-1-phenyl-2-pyrazolin-3-carboxylic acid connected through anthracene and thiophene  $\pi$ -spacers were synthesized and applied in dye-sensitized solar cells. The photophysical and electrochemical properties of these dyes were investigated and their performance as sensitizers in dye-sensitized solar cells was evaluated. Electrochemical studies showed that the lowest unoccupied molecular orbital energy levels can be tuned by introduction of various anchoring groups with different electron withdrawing abilities. The power conversion efficiencies of the dye-sensitized solar cells based on D1–D3 decreased as the electron withdrawing ability of their anchoring groups increased in the order D1 < D2 < D3. The D1-based device showed the highest power conversion efficiency (1.27%).

Keywords: Dye-Sensitized Solar Cells, Anchoring Group, Anthracene, Triphenylamine.

### **1. INTRODUCTION**

Increased emission of greenhouse gases owing to combustion of fossil fuels since the commencement of the industrial revolution has caused the global climate to change more drastically than recorded in history. One of the most critical challenges in modern science is meeting energy demands. In this regard, renewable energy sources have continued to attract attention. Dye-sensitized solar cells (DSSCs) are considered a possible answer to the energy demands because of their high photovoltaic performance, easy fabrication, and low cost of production compared with other solar cells.<sup>1-3</sup> Among the constituents of DSSCs, the dye-sensitizer is a key element for achieving high photovoltaic performance. Years of investigation have led to the development of a plethora of dye-sensitizers, including zinc-based porphyrin sensitizers, polypyridyl ligated ruthenium-complexes, and organic dyes.4-21 However, the cost of noble metals, complex and expensive purification processes, and environmental issues are the main

impediments to the application of ruthenium and zincbased dye-sensitizers; moreover, the conversion efficiencies of these species are far below ideal. Therefore, the development of dye-sensitizers still remains a challenge for further improvement of DSSCs.<sup>22</sup>

Organic dye-sensitizers comprise a donor, a  $\pi$ -bridge/spacer, and an acceptor/anchoring unit, and this structure (D- $\pi$ -A) is related to the potent intramolecular charge transfer (ICT), thereby resulting in facile charge transfer from the excited dye sensitizer (via the anchoring unit) to the semiconductor surface.<sup>23</sup> For an excellent dye-sensitizer, selecting a proper anchoring unit is highly crucial as the anchoring unit determines the binding strength of the dye-sensitizer on the semiconductor surface and thus influences the charge transfer rate.<sup>24, 25</sup> In most organic dye-sensitizers, 2-cyanoacetic acid (CA) is employed in the D- $\pi$ -A structure as an anchoring unit. There are a few reports on the effect of different anchoring units on the D- $\pi$ -A structure.

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As we discussed above, the D- $\pi$ -A system is the basic feature for most organic dyes due to the effective

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J. Nanosci. Nanotechnol. 2017, Vol. 17, No. 11

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Figure 1. Chemical structures of dye sensitizers D1-D3.

intramolecular charge transfer property. Appropriate use of electron-excessive  $\pi$ -bridge between D and A was reported to be advantageous to red shift the charge transfer absorption band. Heo et al. reported anthracene mediated photosensitizers and achieved an efficiency of 3.34%.<sup>26</sup> Teng et al. utilized anthracene as an effective  $\pi$ -spacer between triphenylamine donor and typical cyanoacetic acid acceptor. One of the dyes attained a notable efficiency of 7.03%.15 Herein, for DSSC applications, we synthesize three organic dyes for which the charge-transfer chromophoric system includes triphenvlamine as the donor group with different acceptors. Anthracene and thiophene conjugate groups are inserted between the donor and acceptor units as the  $\pi$ -spacers to extend the  $\pi$ -conjugation, which is expected to enhance the light-harvesting effect. CA, rhodanine-3-acetic acid (RA) and 5-oxo-1-phenyl-2-pyrazolin-3-carboxylic acid (OPCA) are employed as anchoring groups. Figure 1 shows the corresponding dye molecular structures. The ultraviolet-visible (UV-vis), electrochemical, incident photon-to-current conversion efficiency (IPCE), and current density-photovoltage (J-V) properties are also analyzed.

### 2. EXPERIMENTAL DETAILS 2.1. Materials and Instruments

All reactions were carried out under nitrogen atmosphere. The solvents were distilled using appropriate reagents. All starting materials and reagents were purchased from Sigma–Aldrich, TCI, and ACROS Co. <sup>1</sup>H spectra were recorded on a Varian Mercury NMR 300 MHz spectrometer. The chemical shifts are reported in parts-per-million, down-field from tetramethylsilane (TMS) as an internal standard; measurements were performed using appropriate deuterated solvents. The optical spectra of the dyes in solution were recorded with an Agilent 8453 UV-vis spectrophotometer. The electrochemical data were recorded using a CV-BAS-Epsilon instrument. Cyclic voltammograms were obtained from a three electrode cell using 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> chloroform solution and a scan rate of 100 mV s<sup>-1</sup>; Pt wire was used as a counter electrode and Ag/AgCl as the reference electrode. Electrochemical impedance spectroscopy (EIS) was carried out using a computer-controlled potentiostat (IVIUMSTAT, IVIUM).

### 2.1.1. 4-Bromo-N,N-Diphenylaniline (1)

In a three-necked, oven-dried, 150 mL round-bottom flask, triphenylamine (3.000 g, 12.244 mmol) was dissolved in 50 mL of anhydrous chloroform, covered with aluminum foil, and stirred at 25 °C under inert atmosphere for 15 min. *N*-Bromosuccinimide (1.96 g, 11.121 mmol) was then added in small portions, and the resulting solution was stirred at 25 °C for 5 h. The reaction mixture was extracted three times with chloroform. The combined organic fractions were washed with brine and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was re-crystallized by using ethanol to give a white powder (3.020 g, 76%). <sup>4</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.62–7.21 (*m*, 7H), 7.19–7.00 (*m*, 5H), 6.99–6.93 (*m*, 2H).

### 2.1.2. N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)Aniline (2)

Under inert atmosphere, a degassed solution of **1** (3.000 g, 9.250 mmol), bis(pinacolato)diboron (3.054 g, 12.255 mmol), KOAc (3.018 g, 32.225 mmol), and Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (0.338 g, 0.05 mmol) in dry dimethoxyethane (30 mL) was heated under reflux conditions for 15 h. After this period, the mixture was cooled to room temperature, filtered, and diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic solution was washed with H<sub>2</sub>O (2 × 30 mL) and brine, then dried (with anhydrous MgSO<sub>4</sub>) and evaporated. The residue was separated by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> (9/1 v/v) to give compound **2** as a white solid product (2.170 g, 63%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.74–7.59 (d, 2H), 7.19–7.08 (d, 4H), 7.07–6.90 (t, 4H), 1.48–1.16 (t, 12H).

### 2.1.3. 5-(10-Bromoanthracen-9-yl)Thiophene-2-Carbaldehyde (3)

A 50 mL three neck round bottom flask was charged with 10-bromoanthracen-9-boronic acid (0.770 g, 2.000 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.232 g, 10 mol%), tetrahydrofuran (THF; 20 mL) and 2 M aqueous  $K_2CO_3$  (2 mL). The flask was then purged with nitrogen gas for five evacuate/refill cycles. 5-Bromo-2-thiophenecarboxaldehyde (0.460 g,

J. Nanosci. Nanotechnol. 17, 8053-8060, 2017



Thuy et al.

2.400 mmol) was then added under inert atmosphere. The tube was sealed and heated at 70 °C with vigorous stirring for 15 h. Upon cooling to ambient temperature, the organics were extracted three times with  $CH_2Cl_2$ . The combined organic fractions were washed with brine and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> (8/2, v/v) as the eluent to give a yellow powder (0.420 g, 57%). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ): 10.14 (*s*, 1H), 8.7–8.62 (*d*, 2H), 8.25 (*d*, 2H), 7.88–7.77 (*m*, 4H), 7.68–7.57 (*t*, 2H), 7.53–7.46 (*d*, 1H).

### 2.1.4. 5-(10-(4-(Diphenylamino)phenyl)anthracen-9-yl) Thiophene-2-Carbaldehyde (4)

A mixture of compound 3 (0.918 g, 2.500 mmol), compound 2 (0.900 g, 2.500 mmol) and K<sub>2</sub>CO<sub>2</sub> (1.029 g, 8.75 mmol) in toluene/ethanol (15/5 mL) was combined with  $Pd(PPh_3)_4$  (0.347 mg, 0.3 mmol) by addition of the latter under inert atmosphere. After stirring for 24 h at 110 °C, water (10 mL) and dichloromethane (30 mL) were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane  $(2 \times 10 \text{ mL})$ . The organic layer and the dichloromethane extracts were combined and dried (over anhydrous MgSO<sub>4</sub>), and then filtered. The organic solvent was completely removed by rotary evaporation. The solid residue was purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> (8/2, v/v) as the eluent to give a pale yellow solid (0.916 g, 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 10.08 (s, 1H), 8.21–7.97 (d, 1H), 7.90–7.75 (m, 5H), 7.50–7.40 (t, 5H), 7.39–7.20 (m, 10H), 7.15-7.02 (t, 3H).

### 2.1.5. (Z)-2-Cyano-3-(5-(10-(4-(diphenylamino)phenyl) anthracen-9-yl)thiophen-2-yl)Acrylic Acid (D1)

Compound **4**, 5-(10-(4-(diphenylamino)phenyl)anthracen-9-yl)thiophene-2-carbaldehyde (0.100 g, 0.188 mmol) was dissolved in acetic acid (15 mL) and combined with cyanoacetic acid (0.032 g, 0.376 mmol) in the presence of ammonium acetate (0.029 g, 0.376 mmol). The reaction mixture was then refluxed for 5 h under inert atmosphere. After cooling to room temperature, the reaction mixture was poured into crushed ice and the solid obtained was washed thoroughly with water to remove the excess acetic acid and cyanoacetic acid. The solid was washed with hexane to afford a yellow colored solid D1 (0.045 g, 40%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ) 8.27 (*s*, 1H), 8.00 (*s*, 1H), 7.89–7.72 (*t*, 5H), 7.48–7.34 (*m*, 8H), 7.33–7.20 (*t*, 7H), 7.19–7.10 (*m*, 3H).

### 2.1.6. (Z)-2-(5-((5-(10-(4-(Diphenylamino)phenyl) anthracen-9-yl)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)Acetic Acid (D2)

The procedure used for synthesis of compound D1 was followed for synthesis of D2, where the rhodanine-3-acetic

J. Nanosci. Nanotechnol. 17, 8053-8060, 2017

acid (0.036 g, 0.376 mmol) anchoring group was used to afford D2 (0.115 g, 86%) as a dark yellow solid. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ): 8.36 (*s*, 1H), 8.12 (*s*, 1H), 7.81 (*m*, 3H), 7.67–7.55 (*m*, 3H), 7.47–7.14 (*m*, 15H), 4.75 (*s*, 2H).

### 2.1.7. (E)-4-((5-(10-(4-(Diphenylamino)phenyl) anthracen-9-yl)thiophen-2-yl)methylene)-5-Oxo-1-Phenyl-4,5-Dihydro-1H-Pyrazole-3-Carboxylic Acid (D3)

The procedure used for synthesis of compound D1 was followed. The 5-oxo-1-phenyl-2-pyrazolin-3-carboxylic acid (0.076 g, 0.376 mmol) anchoring group was used to afford D3 (0.073 g, 54%) as a red solid. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ): 9.39 (*s*, 1H), 8.42 (*s*, 1H), 8.10-7–7.90 (*m*, 7H), 7.89–7.75 (*m*, 9H), 7.65–7.00 (*m*, 12H).

### 2.1.8. Assembly and Characterization of DSSCs

Transparent conducting glass substrates were cleaned sequentially with ethanol, deionized (DI) water, and acetone under ultrasonication. Nanocrystalline TiO<sub>2</sub> paste was synthesized using ethyl cellulose (Aldrich), lauric acid (Fluka, City, State, Country), and terpineol (Aldrich). TiO<sub>2</sub> particles (ca. 20-30 nm in diameter) were used. The prepared TiO<sub>2</sub> paste was doctor-bladed onto the pre-cleaned glass substrates, followed by drying at 70 °C for 30 min and 30 min of calcination at 500 °C. A scattering layer consisting of rutile  $TiO_2$  particles (250 nm in a size) was deposited on the mesoporous TiO<sub>2</sub> films. These layers were dipped into an aqueous solution of TiCl<sub>4</sub> (0.04 M) at 70 °C for 30 min. The sensitizers were dissolved in dry chloroform (0.2 mM) at 25 °C and stirred for 24 h. The annealed TiO<sub>2</sub> electrodes were dipped in the dye solutions for 18 h.

Pt counter electrodes were prepared by thermal reduction of the films dip-coated in  $H_2PtCl_6$  (7 × 10<sup>-3</sup> M) in 2-propanol at 400 °C for 20 min. The dye-adsorbed TiO<sub>2</sub> and Pt counter electrodes were sandwiched between a  $60 \times 10^{-6}$  m thick Surlyn (Dupont 1702) layer, which was used as a bonding agent and spacer. An  $I^-/I_3^-$  redox couple composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.06 M NaI, 0.04 M I<sub>2</sub>, and 0.4 M 4-tert-butylpyridine in dried CH<sub>3</sub>CN was then introduced through a hole on the Pt counter electrode. The complete device structure was shown in Figure 2. The active area of the dye-adsorbed TiO<sub>2</sub> films was estimated using a digital microscope camera with image-analysis-software (Moticam 1000). The photovoltaic I-V characteristics of the prepared DSSCs were measured under 1 sunlight intensity (100 mW cm<sup>-2</sup>, AM 1.5), which was verified with an AIST-calibrated Sisolar cell (PEC-L11, Peccell Technologies, Inc., City, State, Country). The incident photon-tocurrent efficiencies (IPCEs) were plotted as a function of the light wavelength using an IPCE measurement instrument (PEC-S20, Peccell Technologies, Inc.).

## Glass FTO Electrolyte Dyes TiO<sub>2</sub> FTO Glass

Figure 2. Schematic diagram of the DSSC device.

### 3. RESULTS AND DISCUSSION

### 3.1. Design and Synthesis

In organic dyes, the introduction of a powerful electron withdrawing moiety near the anchoring unit is required to skew the electron density away from the donor segment, thereby lowering the energy bandgap, which shifts the optical spectra to the lower energy regime and is expected to aid electron transport to the TiO<sub>2</sub> semiconductor. This situation has been observed for diverse organic D- $\pi$ -A dyes.<sup>27–29</sup> In most organic D- $\pi$ -A dyes, the presence of cyanoacetic acid (which is prone to *cis-trans* isomerization upon photo-irradiation) near the anchoring region results in enhanced recombination currents.<sup>30</sup> Elimination of such anchoring units could enhance the planarity of the chromophore and might aid in diminishing the recombination. Hence, substituting the cyanoacetic acid acceptor with an

different acceptor in these D- $\pi$ -A chromophores may provide useful information about the importance of acceptor units proximal to the anchoring unit in modifying the photophysical, electrochemical, and photovoltaic performance. Herein, three anthracene/triphenylamine-based organic dyes, D1, D2, and D3, having different acceptors, such as 2-cyanoacetic acid (CA), rhodanine-3-acetic acid (RA) and 5-oxo-1-phenyl-2-pyrazolin-3-carboxylic acid (OPCA), were prepared as sensitizers for TiO<sub>2</sub>based DSSCs. Scheme 1 shows the route for preparation of the new sensitizers. Firstly, simple triphenylamine was brominated using N-bromosuccinimide in chloroform, followed by Suzuki-Miyaura borylation using bis(pinacalato)diboron to obtain intermediate 2. In another step, we started with 10-bromoanthracen-9-boronic acid, which was subjected to Suzuki coupling using 5-bromo-2-thiophenecarboxaldehyde to obtain intermediate 3. The intermediates 2 and 3 were then subjected to Suzuki coupling to obtain the aldehyde intermediate 4. Finally, intermediate 4 was subjected to Knoevenagel condensation using 2-cyanoacetic acid, rhodanine-3-acetic acid, and 5-oxo-1-phenyl-2-pyrazolin-3-carboxylic acid, respectively, to obtain the final target dye-sensitizers D1, D2, and D3.

### **3.2. Optical Properties**

mophore and might aid in diminishing the recombination. Sat The UV-vis absorption spectra of the dyes (D1–D3) in Hence, substituting the cyanoacetic acid acceptor with an solution and on the photoelectrode film (Figs. 3(a and b))





### J. Nanosci. Nanotechnol. 17, 8053-8060, 2017



**Figure 3.** UV-vis absorption spectra of dye sensitizers D1–D3 (a) in solution (dichloromethane); (b) on  $TiO_2$  film.

were acquired, given that the overlap between the spectral profile of the dyes and the solar emission spectrum has a significant impact of the cell photocurrent. The corresponding data are listed in Table I.

The three dyes had a strong absorption band in the visible region, corresponding to intramolecular charge transfer between the donor units and acceptor groups (Fig. 3 and Table I). As shown in Figure 3, D1 exhibited an absorption maximum at 400 nm with a molar extinction coefficient ( $\varepsilon$ ) of 16455 M<sup>-1</sup> cm<sup>-1</sup>. Compared to the absorption maximum of D1, the absorption pattern of D2 was bathochromically shifted by 14 nm, with an absorption maximum at 414 nm ( $\varepsilon = 42675$  M<sup>-1</sup> cm<sup>-1</sup>) because of

 
 Table I.
 Photophysical and electrochemical data for dye sensitizers D1–D3.

Dye	$\varepsilon_{\rm max}~({ m M}^{-1}~{ m cm}^{-1})$	$\lambda_{\max}$ (nm) Sol. TiO <sub>2</sub>	$E_{\rm ox}$ (V)	$E_{\mathrm{ox}}^{*}$ (V)	$E_{0-0}$ (V)
D1	16455	400 402	1.14	-1.52	2.66
D2	42675	414 446	1.15	-1.28	2.43
D3	22675	404 400	1.16	-1.03	2.19
TC401 <sup>15</sup>	12100	402 400	1.17	-1.48	2.65

J. Nanosci. Nanotechnol. 17, 8053-8060, 2017

the replacement of cvanoacetic acid with rhodanineacetic acid having more extended conjugation and a strongly withdrawing acceptor. Similarly, the replacement of CA in D1 with another acceptor group, OPCA, to give D3 resulted in spectral broadening and an increased  $\varepsilon$  of 22675  $M^{-1}$  cm<sup>-1</sup> with an absorption maximum at 404 nm. This decrease in the energy gap is highly advantageous for enhancing the light harvesting ability of the sensitizers. Notably, D2 and D3 exhibited broader peaks and higher  $\varepsilon$ values than obtained for D1. Figure 3(b) shows the absorption spectra of the corresponding dyes on TiO<sub>2</sub> film. The absorption spectra of all three dyes were broadened compared to the corresponding solution spectra (Fig. 3(a)); this is attributed to electronic coupling of the dyes with the  $TiO_2$  surface and possibly some dye aggregation. This phenomenon has been observed for many organic dyes on TiO<sub>2</sub> films. From Figure 3(a),  $E_{0-0}$  values of 266, 2.43, and 2.19 eV were calculated for D1-D3, respectively.

### **3.3. Electrochemical Properties**

The cyclic voltammograms of D1–D3 were acquired in a 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> solution (Fig. 4). The data were used to calculate the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to investigate the regeneration of the dyes from the redox electrolyte and electron transfer from the excited dye-sensitizer to the conduction band of the TiO<sub>2</sub> semiconductor, respectively. Generally, the for-

mal oxidation potentials correspond to the HOMO level of the dye-sensitizer and the LUMO values are calculated from the difference between  $E_{ox}$  and  $E_{0-0}$ , where the  $E_{0-0}$  values are determined from the onset absorption spectra (Fig. 3(a)). The HOMO, LUMO, and  $E_{0-0}$ values are summarized in Table I. The HOMO levels of the dyes were in the range of 1.14–1.16 V; these values are more positive than that of the  $I^-/I_3^-$  redox electrolyte (~0.4 V vs. NHE).<sup>28</sup> For comparison, optical and electrochemical data of structurally similar dye TC401



Figure 4. Cyclic voltammograms of dye sensitizers D1-D3.

Effect of Anchoring Group in Anthracene/Thiophene-Bridged Triphenylamine-Based Organic Dyes for DSSCs

were shown in Table I.<sup>15</sup> This suggests that the oxidized dye can be regenerated via electron donation from the I<sup>-</sup> ions in the I<sup>-</sup>/I<sub>3</sub><sup>1</sup> redox electrolyte. Further, the calculated LUMO values (Table I) were more negative than the conduction band edge of the TiO<sub>2</sub> semiconductor ( $\sim -0.5$  V vs. NHE),<sup>28</sup> suggesting that the excited electrons are efficiently injected into the conduction band of TiO<sub>2</sub>. The strong electron-withdrawing acceptors such as RA and OPCA could positively shift the reduction potential of D2 and D3 compared to that of D1 having the less electron-withdrawing CA acceptor unit. This could lead to lowering of the LUMO level of the dye, resulting in a lower thermodynamic driving force for electron injection.

### **3.4.** Photovoltaic Properties

Figure 5 presents the incident photon-to-current conversion efficiency (IPCE) of the devices based on dyes D1-D3. D1 with CA as the acceptor showed a stronger solar cell response in the 350-550 nm spectral region, compared to that of the other dyes with RA and OPCA as acceptors. The device with D1 showed plateaus of more than 40% from 350-470 nm with the highest value at 418 nm and an onset at 550 nm. The onset of the IPCE for D2 and D3 was extended to 600 nm, which corresponds to a bathochromic shift of 50 nm compared to that of D1. The difference between the IPCE spectra of the studied dyes is in good agreement with their optical absorption spectra (Fig. 3). The relatively higher IPCE values for D1 led to higher  $J_{sc}$  values compared with those of D2 and D3. Although D2 and D3 have a broader and higher absorption in all regions, in comparison with dye D1, the DSSCs based on D2 and D3 had a lower IPCE. This might be caused by the lower electron injection caused by the lower LUMO levels.

Figure 6 presents the current density-photovoltage (J-V) characteristics of the devices using D1-D3 and



Figure 5. IPCE spectra for the DSSCs based on dye sensitizers D1–D3.



Figure 6. J-V curves for the DSSCs based on dye sensitizers D1-D3.

Table II lists the corresponding photovoltaic parameters. For comparison, the photovoltaic performance of the structurally similar dye TC401 included in Table II.<sup>15</sup> The device based on D1 showed better photovoltaic performance with a photo-current density ( $J_{sc}$ ) of 3.12 mA cm<sup>-2</sup>, an open circuit photovoltage ( $V_{oc}$ ) of 0.607 V, and a fill factor (FF) of 66.88, corresponding to a power conversion efficiency ( $\eta$ ) of 1.27%.

Upon replacing the CA acceptor with the RA acceptor, the power conversion efficiency of the D2-based device declined to 0.91% due to a drop of the  $J_{sc}$  from 3.12 mA cm<sup>-2</sup> to 2.84 A cm<sup>-2</sup>. Previously, molecular modeling studies showed that the acceptor CA induces a vertically oriented dye geometry when it is attached to a semiconductor surface, whereas the donor part of the RA acceptor-based dye was aligned in close proximity to the semiconductor surface at a tilted angle. Hence, it was concluded that the dye cation with the RA group as an acceptor unit was prone to undergo more inner-path recombination with the injected electrons.<sup>31–33</sup> The  $J_{sc}$  and efficiency decreased further to  $1.78 \text{ mA cm}^{-2}$  and 0.70%, respectively, for the device with D3, where the CA acceptor group was replaced with the OPCA acceptor. This might be partially attributed to the poor electron injection efficiency, as evidenced in the above section. On the other hand, compared to the D1-based device with a  $V_{oc}$  of 0.607 V, the D2 and D3-based devices exhibited considerably lowered  $V_{\rm oc}$  values of 0.485 and 0.541 V, respectively, possibly due to the tilted orientation on the semiconductor

**Table II.** Photovoltaic data for the DSSCs based on dye sensitizers D1–D3 and reference N719.

Dve	$I (mA \text{ cm}^{-2})$	$V_{\rm V}$ (V)	FF (%)	$\eta~(\%)$
Dye	$J_{\rm sc}$ (IIIA CIII )	V <sub>oc</sub> (V)	11 (70)	
N719	15.35	0.670	66.62	6.84
D1	3.19	0.607	66.88	1.27
D2	2.84	0.484	66.13	0.91
D3	1.78	0.541	73.33	0.70
TC40115	5.39	678	79.7	2.91

J. Nanosci. Nanotechnol. 17, 8053-8060, 2017



Figure 7. EIS spectra of the dye sensitizers D1–D3.

surface, which could lead to inner-path recombination.<sup>31-33</sup> Moreover, the presence of strong electron withdrawing groups, such as RA or OPCA (compared to CA), near the anchoring group is thought to be detrimental to charge entrapment around the withdrawing group, and consequently to the electron injection efficiency or recombination. Because of the strongly electron withdrawing nature of the RA and OPCA groups, D2 and D3 showed lowered light-to-electricity energy conversion efficiency compared to D1, despite their superior light harvesting ability.

To further understand the working electrode interface, we performed electrochemical impedance spectroscopy studies (EIS) since this technique has been a useful tool to estimate charge transfer resistance and to know the dye regeneration efficiency. Figure 7 shows EIS results for DSSCs comprised of D1–D3 under illuminated conditions. The radius of the semicircle corresponding to the working electrodes of these dyes are in the order of D3 > D2 > D1. The introduction of RA and OPCA anchoring groups largely increases the charge transfer resistances. The increase of charge transfer resistance value would affect the photo-regeneration resulting in inferior performance. The fitting data of EIS agreed well with photovoltaic performance shown in Figures 5 and 6, and Table II.

### 4. CONCLUSION

Three triphenylamine-based metal-free organic dyes (D1–D3) with different anchoring groups (CA, RA, and OPCA) bridged by anthracene- and thiophenecontaining  $\pi$ -spacers were synthesized for application in dye-sensitized solar cells. Specific analyses of the relationship between the dye structure, absorption properties, electrochemical properties, photocurrent–voltage, and incident photon-to-current conversion efficiency were performed. Despite the broader IPCE, D2 and D3 showed decreased IPCE values, possibly due to the lower LUMO levels and charge entrapment around the strong withdrawing groups. The overall power conversion efficiency of the DSSC based on D1 with the CA anchoring group (1.27%) was higher than that of the other dyes. Overall, the data demonstrate that the introduction of different anchoring groups with different withdrawing abilities has a significant effect on the power conversion efficiency of DSSCs.

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### **References and Notes**

- 1. B. O'Regan and M. Gratzel, Nature 353, 737 (1991).
- A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Chem. Rev.* 110, 6595 (2010).
- 3. M. Graetzel, Nature 414, 338 (2001).
- S. Mathew, A. Yella, P. Gao, R. H. Baker, B. F. Curchod, N. A. Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, and M. Grätzel, *Nat. Chem.* 6, 242 (2014).
- A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, and M. Grätzel, *Science* 334, 629 (2011).
- 6. L. L. Lia and E. W. G. Diau, Chem. Soc. Rev. 42, 291 (2013).
- B. Pashaei, H. Shahroosvand, M. Graetzel, and M. K. Nazeeruddin, Chem. Rev. 116, 9485 (2016).
- T. Suresh, G. Rajkumar, S. P. Singh, P. Y. Reddy, A. Islam, L. Han, and M. Chandrasekharam, *Org. Electron.* 14, 2243 (2013).
- 9. D. K. Lee, K. S. Ahn, S. Thogiti, and J. H. Kim, *Dyes Pigm.* 117, 83 2(2015): 2018 16:00:12
- 10. T. Suresh, K. Ganesh, S. P. Singh, A. Islam, L. Han, and M. Chandrasekharam, *Dyes Pigm.* 99, 850 (2013).
- A. Mishra, M. K. R. Fischer, and P. Bäuerle, *Angew. Chem. Int. Ed.* 48, 2474 (2009).
- Y. H. Lee, R. K. Chitumalla, B. Y. Jang, J. Jang, S. Thogiti, and J. H. Kim, *Dyes Pigm.* 133, 161 (2016).
- 13. T. H. Nguyen, T. Suresh, and J. H. Kim, Org. Electron. 30, 40 (2016).
- 14. H. Jia, K. Shen, X. Ju, M. Zhang, and H. Zheng, New J. Chem. 40, 2799 (2016).
- C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt, and L. C. Sun, J. Phys. Chem. C 114, 9101 (2010).
- 16. C. L. Wang, P. T. Lin, Y. F. Wang, C. W. Chang, B. Z. Lin, H. H. Kuo, C. W. Hsu, S. H. Tu, and C. Y. Lin, *J. Phys. Chem. C* 119, 24282 (2015).
- W. Zeng, Y. Cao, Y. Bai, Y. Yang, Y. Shi, M. Zhang, F. Wang, C. Pan, and P. Wang, *Chem. Mater.* 22, 1915 (2010).
- 18. J. S. Ni, Y. C. Yen, and J. T. Lin, J. Mater. Chem. A 4, 6553 (2016).
- V. K. Singh, R. K. Kanaparthi, and L. Giribabu, *RSC Adv.* 4, 6970 (2014).
- K. Ramavenkateswari and P. Venkatachalam, *Electron. Mater. Lett.* 12, 628 (2016).
- P. Ho, S. Thogiti, Y. H. Lee, and J. H. Kim, Sci. Reports 7, 2272 (2017).
- 22. C. P. Lee, R. Y. Y. Lin, L. Y. Lin, C. T. Li, T. C. Chu, S. S. Sun, J. T. Lin, and K. C. Ho, *RSC Adv.* 5, 23810 (2015).
- X. Zhang, J. Mao, D. Wang, X. Li, J. Yang, Z. Shen, W. Wu, J. Li, H. Ågren, and J. Hua, ACS Appl. Mater. Interfaces 7, 2760 (2015).
- 24. L. Zhang and J. M. Cole, ACS Appl. Mater. Interfaces 7, 3427 (2015).
- 25. F. Ambrosio, N. Martsinovich, and A. Troisi, J. Phys. Chem. Lett. 3, 1531 (2012).

J. Nanosci. Nanotechnol. 17, 8053-8060, 2017

- 26. D. U. Heo, S. J. Kim, B. J. Yoo, B. Kim, M. J. Ko, M. J. Cho, and D. H. Choi, *Bull. Korean Chem. Soc.* 34, 1081 (2013).
- P. Ganesan, A. Yella, T. W. Holcombe, P. Gao, R. Rajalingam, S. A. Al-Muhtaseb, M. Graetzel, and M. K. Nazeeruddin, ACS Sustainable Chem. Eng. 3, 2389 (2015).
- 28. H. J. Ahn, T. Suresh, J. M. Cho, B. Y. Jang, and J. H. Kim, *Electron. Mater. Lett.* 11, 822 (2015).
- 29. J. H. Park, B. Y. Jang, S. Thogiti, J.-H. Ryu, S.-H. Kim, Y.-A. Son, and J. H. Kim, *Synth. Met.* 203, 235 (2015).
- B. Zietz, E. Gabrielsson, V. Johansson, A. M. El-Zohry, L. Sun, and L. Kloo, *Phys. Chem. Chem. Phys.* 16, 2251 (2014).
- **31.** B.-G. Kim, K. Chung, and J. Kim, *Chem. Eur. J.* 19, 5220 (2013).
- 32. H. Tian, X. Yang, R. Chen, Y. Pan, L. Li, A. Hagfeldt, and L. Sun, *Chem. Commun.* 36, 3741 (2007).
- 33. J. Wiberg, T. Marinado, D. P. Hagberg, L. Sun, A. Hagfeldt, and B. Albinsson, J. Phys. Chem. C 113, 3881 (2009).

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