#### Dyes and Pigments 96 (2013) 313-318

Contents lists available at SciVerse ScienceDirect

**Dyes and Pigments** 

journal homepage: www.elsevier.com/locate/dyepig

## New *N*-methyl pyrrole and thiophene based D $-\pi$ -A systems for dye-sensitized solar cells

### Bo Hyung Kim, Harold S. Freeman\*

Fiber and Polymer Science Program, North Carolina State University, Raleigh, NC 27695, USA

#### ARTICLE INFO

Article history: Received 23 July 2012 Received in revised form 1 September 2012 Accepted 4 September 2012 Available online 12 September 2012

Keywords: DSSCs Heterocyclic spacers Recombination lifetime D $-\pi$ -A system IPCE TiO<sub>2</sub> film

#### ABSTRACT

Dye-sensitized solar cells (DSSCs) containing novel DP-T and DP-P organic sensitizers having thiophene and N-methyl pyrrole moieties as  $\pi$  bridges in a D- $\pi$ -A system were assembled and characterized. Incorporation of a thiophene bridge to give sensitizer **DP-T** enhanced solar energy capture, while impedance spectroscopy showed a much longer electron recombination lifetime ( $\tau$ ) for the DSSCs based on pyrrole containing sensitizer **DP-P**. The observed kinetics led to increased open circuit voltage ( $V_{oc}$ ) for the device based on **DP-P**, regardless of types of additives (TBP or DCA) employed in the devices. Better photovoltaic performance was achieved using DP-T.

© 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Dye-sensitized solar cells (DSSCs) are of great interest because their construction involves low cost components and they are relatively simple, affording them the potential to compete with fossil fuel-based electricity generation, a non-renewable process. Ru (II) based polypyridyl complexes for DSSCs attracted early attention in this arena, by giving a photon-to-current conversion efficiency ( $\eta$ ) of ~12% [1]. Studies aimed at metal-free dye sensitizers led to merocyanine [2], oligoene [3,4], coumarin [5,6], indoline [7,8], and cyanine dyes [9,10], with an efficiency ( $\eta$ ) up to 10% achieved by using metal-free dye C219 containing ethylenedioxothiophene and dithienosilole blocks [11]. Although the performance of DSSCs based on metal-free organic dyes has not exceeded that of solar cells based on Ru-complexed dyes, metalfree types remain of interest for DSSCs due to advantages that include high absorption coefficients resulting from intramolecular  $\pi - \pi^*$  transitions, straightforward synthesis, color tuning, structural modification for desired physical and photochemical properties, and their economy. Typical metal-free sensitizers are based on

# HOMO/LUMO energy levels and/or spectroscopic properties [14]. Generally, increased conjugation path length using oligoene [4] or

oligothiophene [5] was adopted as a basic way to achieve a red shift. However, a flexible extended chain length had a negative effect on charge separation or efficient generation of photons, thus counteracting the positive effect of red shifted absorption spectra contributing to large solar capture [15]. On the other hand, it was reported that the presence of a rigid spacer [16,17] or introduction of an alkyl group [18] as a side chain affected dye aggregate and/or charge recombination and, consequently, photovoltaic performance. Results from another recent study showed that the even a small change in the bridging unit caused a significant change in photovoltaic parameters [19]. In addition, aryl amine based donors [20,21] have been used to give efficient charge separation and/or control charge recombination. In view of these different results, the rigid N-methyl pyrrole system, having both electron rich character and low delocalization energy [22], attracted our attention and led us to investigate its effect on photovoltaic parameters relative to the thiophene ring system commonly incorporated into DSSC

a donor-spacer-acceptor system (D- $\pi$ -A), to achieve effective charge separation and transfer. Molecular engineering of donor

groups has evolved from the use of a simple triphenylamine moiety to a starburst phenylene based moiety [12,13], to control electronic

levels or molecular geometry and to afford effective charge transfer.

A  $\pi$  bridging unit has been a common design feature, to influence





<sup>\*</sup> Corresponding author. Tel.: +1 919 515 6552; fax: +1 919 515 3057.

E-mail addresses: bkim6@ncsu.edu (B.H. Kim), hfreeman@ncsu.edu, harold\_ freeman@ncsu.edu (H.S. Freeman).

<sup>0143-7208/\$ -</sup> see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2012.09.001

sensitizers. The present paper reports the photovoltaic performance of DSSCs sensitized with two new metal-free sensitizers in which a diphenylamino-substituted indole moiety and cyanoacrylic acid were connected using either thiophene or *N*-methyl pyrrole to form a  $D-\pi-A$  system (cf. Fig. 1), as a part of a larger study in which heterocyclic systems in place of a benzene spacer and a bulky *bis*-carbazoleaminor donor in place of diphenylamine were examined for DSSC dye development [23].

#### 2. Methods

#### 2.1. Materials

All reagents were purchased from Sigma—Aldrich, TCI, or Fisher Scientific. All chemicals used in this study were of reagent-grade quality and solvents purchased from commercial suppliers were used without further purification. Moisture-sensitive reactions were performed under either nitrogen or argon gas. All reactions were followed by thin-layer chromatography (TLC) using Analtech silica gel GHLF plates. The N719 sample used for fabrication of the reference solar cell was received as a gift from Dyesol and used without further purification.

#### 2.2. Characterizations

#### 2.2.1. Structure confirmation

<sup>1</sup>H NMR spectra were recorded on a 300, 400, or 500 MHz Bruker Advance spectrometer using DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as a solvent. <sup>13</sup>C NMR spectra were recorded on a 500 MHz Bruker Advance spectrometer. 2-Dimensional NMR spectra including COSY, HSQC, and HMBC were recorded on a 500 MHz or 700 MHz Bruker Advance spectrometer. High resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI), in the positive mode, on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer.

#### 2.2.2. Spectroscopic analysis

UV-Vis spectra in solution and in dye-loaded TiO<sub>2</sub> film were recorded on a Varian Cary 300 UV-Vis spectrophotometer. Photoluminescence of dve solutions was recorded using a fluorometer (Fluorolog<sup>®</sup>-3, HORIBA, USA) equipped with a 450 W xenon lamp (FL-1039/40, HORIBA, USA). The concentration of dye solutions for emission spectra was constrained to have absorbance of  $\sim 0.2$ . Fluorescence lifetime of each dye in THF was measured by a system using a TCSPC (time-correlated single photon counting) controller. LED (NanoLED-460, HORIBA) having a peak wavelength of 460 nm was used as an excitation source and Ludox<sup>®</sup> in distilled water was used as an internal reference. The instrument response was measured below the 200 ns of time period. The decay curve obtained was fitted to the multi-exponential function represented by  $A + B1\exp(-i/T1) + B2\exp(-i/T2)$ . In order to predict the amount of dye adsorbed on the TiO<sub>2</sub> surface, dyes on TiO<sub>2</sub> film were desorbed into a solution of 0.1 M NaOH in THF-H<sub>2</sub>O (v/v, 1:1) followed by measurement of UV-Vis spectra and calculation of the adsorbed amount of dye using Beer-Lambert's law. Thickness of dye loaded TiO<sub>2</sub> film for all characterizations was 6  $\mu$ m.



Fig. 1. Chemical structures of DP-T and DP-P.

#### 2.2.3. Voltammetry and impedance measurements

The oxidation potential of dye adsorbed on  $TiO_2$  films was measured using a three electrode electrochemical cell in acetonitrile containing 0.1 M  $TBAPF_6$  (tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mV s<sup>-1</sup>. Dye coated  $TiO_2$  film was used as a working electrode and Ag/Ag<sup>+</sup> electrode and Pt wire were employed as a reference and counter electrode, respectively. The potential of the working electrode was calibrated with ferrocene as an internal reference.

The impedance spectroscopy of the cell was recorded using an impedance analyzer connected to a potentiostat (reference 600TM, Gamry Instruments, USA) in a frequency range of  $0.1 \text{ Hz}-10^5 \text{ Hz}$  at room temperature under dark condition. The applied forward bias was - 0.65 V and AC amplitude was set to 10 mV.

#### 2.2.4. Photovoltaic measurements

Photocurrent—voltage characteristics of DSSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light coming from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (1 mW/cm<sup>2</sup>). The current—voltage curve of the cell was obtained by applying external voltage bias and the measuring generated photocurrent. The measurement was fully controlled under Oriel IV Test Station software. A mask (0.30 cm<sup>2</sup>) was covered on the testing cell during photocurrent and voltage measurement. The photo active area of cell was  $0.5 \times 0.4$  cm.

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochrometer. Calibration of incident light was performed using a silicone photodiode (IF035, PV Measurements). Monochromatic quantum efficiency was recorded at short circuit conditions under AC mode with white-light bias. Wavelength sampling interval was 10 nm. The beam size of monochromatic light illuminated on DSSCs was  $0.1 \times 0.5$  cm and chopping speed of AC was set to 10 Hz.

#### 2.3. Synthesis of target dye sensitizers

#### 2.3.1. (2E)-2-cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3Hindol-2-yl)thiophen-2-yl)acrylic acid (**DP-T**)

To a solution of compound **1c** (0.3 g, 0.70 mmol) and 2cyanoacetic acid (0.07 g, 0.85 mmol) in acetonitrile (70 ml) was added a few drops of piperidine under N<sub>2</sub> gas flow. The reaction mixture was then stirred under reflux at 80 °C. The precipitate formed during reaction was collected by filtration and dried. Pure **DP-T** was obtained by column chromatography (dichloromethane/ methanol, 12/1, v/v) on silica gel, to give a red solid. Yield: 87%, <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 8.13 (s, 1H), 7.87 (d, 1H, *J* = 3.9 Hz), 7.76 (d, 1H, *J* = 3.6 Hz), 7.54 (d, 1H, *J* = 8.4 Hz), 7.33–7.28 (m, 4H), 7.21 (d, 1H, *J* = 2.1 Hz), 7.06–7.01 (m, 6H), 6.93 (dd, 1H, *J* = 8.2 Hz, 2.1 Hz), 1.47 (s, 6H). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 176.35, 162.84, 148.97, 148.39, 147.44, 145.84, 141.09, 140.07, 139.56, 135.83, 129.54, 129.52, 123.66, 123.56, 122.90, 121.25, 118.83, 117.23, 111.53. HRMS-ESI: calculated for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>S (M + H)/z 490.1584, Found: 490.1579.

#### 2.3.2. (2E)-2-cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3Hindol-2-yl)-1-methyl-1H-pyrrol-2-yl)acrylic acid (**DP-P**)

To a stirred solution of **2d** (0.13 g, 0.31 mmol) and 2-cyanoacetic acid (0.05 g, 0.61 mmol) in ethanol (20 ml) was added NaOH (0.05 g, 1.22 mmol) under N<sub>2</sub> gas flow. The reaction mixture was then stirred under reflux at 80 °C. The mixture formed during reaction was filtered and product was dried. Pure **DP-P** was obtained by

column chromatography (dichloromethane/methanol, 10/1, v/v) on silica gel, to afford an orange-yellow solid. Yield: 34%, <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 8.28 (s, 1H), 7.34 (d, 1H, *J* = 8.4 Hz), 7.30–7.25 (m, 4H), 7.18 (d, 1H, *J* = 2.7 Hz), 7.15 (d, 1H, *J* = 2.1 Hz), 7.02–6.97 (m, 6H), 6.90 (dd, 1H, *J* = 8.4 Hz, 2.4 Hz), 6.80 (d, 1H, *J* = 3.0 Hz), 1.40 (s, 6H). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 179.24, 164.08, 150.06, 148.09, 147.58, 144.32, 140.83, 129.64, 129.41, 129.01, 127.73, 124.11, 123.11, 122.37, 120.27, 119.36, 118.99, 117.90, 109.19, 53.58, 35.94, 24.19. HRMS-ESI: calculated for C<sub>31</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub> (M + H)/z 487.2129, Found: 487.2129.

#### 2.4. Molecular modeling methods

DFT (density functional theory) calculations were conducted using Gaussian 03 software. Geometries were optimized using the B3LYP hybrid functional (Beck's three-parameter functional and Lee–Yang–Parr functional) as an exchange-correlation functional and 3-21G(d) was used as the basis set. HOMO and LUMO orbitals were determined using optimized geometries.

#### 3. Results and discussion

#### 3.1. Modeling studies

Prior to the synthesis of the target dyes, molecular modeling studies involving Gaussian 03 [24] were used to calculate: (1) thermodynamically favorable electron injection into the conduction band edge of  $TiO_2$  and (2) electronic energies and densities at HOMO and LUMO levels. Fig. 2 shows the calculated electronic energies of frontier orbitals and corresponding surface isodensity plots. For both dyes, the  $E_{lumo}$  values were located above the conduction band edge ( $E_{cb}$ ) of TiO<sub>2</sub> (-4.0 eV versus vacuum). The *E*<sub>homo</sub> values were below the energy of the redox species of iodide/ triiodide (-4.8 eV versus vacuum) [25]. It was concluded that these relative matchings of electronic levels of sensitizers would lead to energetically favorable electron injection as well as regeneration of oxidized dye during DSSC operation. Furthermore, HOMO-LUMO excitation moved the electron distribution from the donor side (diarylamine substituted indole moiety) to the acceptor side (the cyanoacrylic acid group), ensuring efficient charge separation by photo-excitation of dye.



**Fig. 2.** Schematic representation of electronic densities, energies, and geometries for **DP-T** and **DP-P**. All parameters were obtained using DFT-B3LYP at 3-21G(d) level. Inset figure (a) and (b) indicate dihedral angles for **DP-T** and **DP-P**, respectively.

#### 3.2. Synthesis

Based on the results of the DFT calculations, target dye sensitizers were synthesized (Fig. 3). Intermediates (i and ii), which underwent Fisher indole cyclization [26], were prepared by the reaction of each heterocyclic starting material with isobutyric anhvdride in the presence of Lewis acid [26,27]. Following Fisher indole cyclization, amination under Buchwald–Hartwig reaction conditions [28] was followed by formylation, which was done by either metal-halogen or metal-hydrogen exchange using n-BuLi [29] for **DP-T**. The two steps were reversed for **DP-P**. Reaction [30] of the formylated intermediate (1c and 2d) with cyanoacetic acid produced the target dyes. 2-Dimensional NMR including COSY (correlation spectroscopy), HSQC (heteronuclear single quantum coherence), and HMBC (heteronuclear multiple-bond correlation spectroscopy) analysis (Supplementary Data S1–S4) allowed us to distinguish the desired structural isomer (ii) from a possible structural isomer of the 2-methyl-(1-(1-methyl-1H-pyrrol-3-yl) propan-1-one).

#### 3.3. Optical and electrochemical properties

The oxidation potential  $(E_{ox})$  of dye sensitizers adsorbed on TiO<sub>2</sub> films was measured with a three electrode electrochemical cell at a scan rate of 100 mV s<sup>-1</sup>. The cyclovoltammogram (Supplementary Data S5) of **DP-T** indicated a one-electron transfer process arising from the oxidation of the diphenylamine moiety of this dye. The corresponding oxidation and reduction potential for DP-T were 1.38 V and -0.92 V versus NHE, respectively. However, the oxidation potential of **DP-P** obtained by cyclovoltammetric technique could not be resolved due to the background charging current. Although DPV (differential pulse voltammetry) might be employed to enhance resolution of the voltammogram [31], given the more electron rich nature of the N-methyl pyrrole ring than the thiophene ring, it is anticipated that the redox potentials of **DP-P** are negatively shifted relative to those of **DP-T**. This is because oxidation of the diarylamine moiety would be enhanced by the introduction of an electron rich moiety. These results are supported by our molecular modeling study, which showed an  $E_{HOMO}$  increase of 33 eV (6 eV for *E*<sub>LUMO</sub>) for **DP-P** compared to the *E*<sub>LUMO</sub> value of **DP-**T. Judging from the electrochemical analysis combined with modeling study, enough driving force was obtained for the electron injection process for both dyes.



**Fig. 3.** Synthetic protocol for **DP-T** and **DP-P**. (a) TsOH·H<sub>2</sub>O at 85 °C. (b) Pd<sub>2</sub>(dba)<sub>3</sub>, X-Phos, sodium tert-butoxide, NHPh<sub>2</sub>, Toluene, 1 day, 80 °C. (c) (i) n-BuLi, THF, -78 °C; (ii) DMF, -78 °C, 1 h; (iii) -78 °C to rt for 2 h; (iv) 10% HCl (d) cyanoacetic acid, piperidine, CH<sub>3</sub>CN, reflux, 3 h (e) NIS, THF, rt, 4 h (f) Pd<sub>2</sub>(dba)<sub>3</sub>, X-Phos, Cs<sub>2</sub>CO<sub>3</sub>, NHPh<sub>2</sub>, Toluene, 1 day, 80 °C.

Fig. 4 provides a schematic representation of possible forward reactions (solid arrows) by photo-excitation of dyes and back electron transfers (dashed arrows) impeding high efficiency of DSSCs.

Related research on the metal-free sensitizers afforded an electron injection time of <100–200 fs (K<sub>2</sub>) and an emission lifetime (B<sub>3</sub>) on a ns scale [4,6,32]. In this study, we examined the relaxation time constants (K<sub>2</sub>) of excited dye sensitizers by time-resolved single photon counting methods (TCSPC) [33]. The decay curves obtained (Supplementary Data Fig. S6) after photo-excitation of dyes was fit to an exponential function:  $F(t) = A + B1 \cdot \exp(-t/T1) + B2 \cdot \exp(-t/T2)$ , where *B* is light intensity and *T* is lifetime obtained. Fitting was repeated until CHISQ ( $\chi^2$ ) value [34] was close to 1 to ensure good fitting of decay curves.

Among the two lifetimes obtained (Supplementary Data Table S1), the lifetime of higher relative amplitude was taken as the lifetime for a given dye. The resultant lifetime constants were 4.11 ns for **DP-T** and 3.55 ns for **DP-P**. Considering the pico or femto second scale of the electron injection process for most metal-free organic dyes [4,6,32,35,36], the relaxation process (Fig. 4, B<sub>1</sub>) of the present dye sensitizers would not hinder electron injection process (Fig. 4, K<sub>2</sub>).

Light absorption phenomena, one of the important features of high efficiency DSSCs were examined using UV-Vis spectroscopy. Absorption (Fig. 5) and emission spectra (Supplementary Data Fig. S7) of the present dye sensitizers were recorded on THF solutions. Among the three absorption peaks for dye **DP-T**, the one in the low energy region was assigned to the ICT (internal charge transfer) band, while peaks in the UV region arose from the localized  $\pi - \pi^*$  transition of the conjugated system [19]. Notably, dye **DP-T** ( $\lambda_{max} = 464 \text{ nm}$ ) having thiophene unit was characterized by a 69 nm bathochromic shift of absorption spectrum compared to that of dye **DP-P** ( $\lambda_{max} = 395 \text{ nm}$ ). **DP-P** hypsochromism might be due to a lower electron push from donor side toward acceptor side in the presence of an electron rich pyrrole ring in this  $D-\pi-A$ system, resulting in an increased energy gap between HOMO and LUMO. Also, **DP-P** hypochromism ( $\varepsilon_{max} = 17,000$ ) arises from the twisted molecular structure induced by steric interactions between *N*-methyl groups and neighboring units. From the investigation of optimized geometries, DP-P exhibited dihedral angles of 17° and 24° with the neighboring indole moiety and anchoring unit, respectively, whereas **DP-T** ( $\varepsilon_{max} = 25,500$ ) showed almost plane geometry (Fig. 2(b)).

Dye adsorption on a  $TiO_2$  surface showed somewhat different absorption spectra than those recorded in solution (Fig. 5). Bare

(B1)

D

load

Dve

Electrolyte

(B<sub>2</sub>)

TiO<sub>2</sub>

Evac(eV)

50





**Fig. 5.** Absorption spectra of dye sensitizers **DP-T** and **DP-P** and dye-loaded  $TiO_2$  film. (Solid, rectangle shaped, and dashed lines indicate the spectra obtained from THF solutions, dye-loaded  $TiO_2$  film, and dye/DCA loaded  $TiO_2$  film, respectively.)

TiO<sub>2</sub> film, which was used as a reference, showed an absorption starting around 380 nm (Supplementary Data S8). DP-T loaded TiO<sub>2</sub> film showed a red-shifted absorption spectrum ( $\lambda_{max} = 476$  nm) with broadened features. This suggests that strong dye-dye interactions or/and dye-TiO<sub>2</sub> interactions are present, leading to dye aggregates on the TiO<sub>2</sub> electrode [37,38]. In the case of **DP-P**, its  $\lambda_{max}$  on TiO<sub>2</sub> film could not be resolved due to the relatively large absorption arising from the bare TiO<sub>2</sub> film. However, it appears that the absorption spectrum of **DP-P** loaded TiO<sub>2</sub> film also gives shifted or broadened feature compared to that in solution, judging from the part of absorption edge above 450 nm. Absorption in this region was not caused by the reference TiO<sub>2</sub> film. In order to gain further insight into the spectral changes of dyes on TiO<sub>2</sub> film, DCA (deoxvcholic acid) [39], a suppressing agent of dve aggregates on  $TiO_2$ films, was co-adsorbed with dyes on the TiO<sub>2</sub> electrode. This caused the absorption maximum of **DP-T**/DCA loaded TiO<sub>2</sub> film to shift toward the one in solution, providing evidence for dye aggregate formation on TiO<sub>2</sub> surface in the absence of DCA (Fig. 5). At the same time, addition of DCA lowered the adsorbed amount of dye on the TiO<sub>2</sub> surface as it competes with dye molecules for TiO<sub>2</sub> sites (Supplementary Data S9). According to the normalization of absorbance of dye/DCA loaded TiO<sub>2</sub> film at a given  $E_{max}$ , the adsorption of DP-T and DP-P was reduced by 5 and 20%, respectively, in the presence of DCA.

Bearing in mind that fast recombination components have been identified as an efficiency-limiting factor, electrochemical impedance spectroscopy (EIS) [31] measured under dark condition would be useful in obtaining the time constant related to a back electron transfer (route B<sub>3</sub> in Fig. 4). To investigate the effects of additives on recombination kinetics, **device B** having DCA and **device C** with 4-tert-butylpyridine (TBP) were fabricated as well as a reference **device A**, which had no additives.

Fig. 6 shows Nyquist plots for these three devices. According to the charge recombination lifetimes ( $\tau$ ) of **device A** extracted from the Nyquist plot, **DP-P** ( $\tau = 40$  ms) showed a 5-fold higher lifetime than **DP-T** ( $\tau = 8$  ms). The superior kinetic properties of devices based on **DP-P** relative to those based on **DP-T** remain consistent regardless of the presence of DCA or TBP. Use of TBP resulted in a much higher  $\tau$ , verifying its effect on controlling  $E_{cb}$  and/or recombination via a surface passivation effect [5,40]. These recombination kinetics were also supported by dark-current measurements (Supplementary Data S10–S11).

Concerning factors affecting  $\tau$  values of DSSCs, factors such as blocking effects, surface coverage [41], or complexation of dyes with oxidizing species in electrolyte [42] have been pointed out. In this regard, **device A** sensitized with **DP-T** (8.79E-0.8 mol/cm<sup>2</sup>) gave higher dye loads on TiO<sub>2</sub> than the device based on **DP-P** (1.16E-07 mol/cm<sup>2</sup>). Assuming that the higher amount of adsorbed **DP-T** could be a result of easier tendency of dye aggregate formation on the TiO<sub>2</sub> surface [6], a device based on **DP-T** might impede efficient



Fig. 6. Electrochemical impedance spectra of DSSCs fabricated with different additives: device A contained 0.6 M DMPII, 0.1 M Lil, 0.05 M I<sub>2</sub>, in dry CH<sub>3</sub>CN; device B was adsorbed with 0.3 mM dye and 1 mM DCA and contained same electrolytes as device A; device C contained 0.6 M DMPII, 0.1 M Lil, 0.05 M I<sub>2</sub>, 0.5 M TBP in dry CH<sub>3</sub>CN.

surface blocking of dyes on TiO<sub>2</sub> electrode. However, this assumes that dye aggregates are adsorbed on TiO<sub>2</sub> surfaces in the form of "highly ordered layers". Furthermore, dye loss by the DCA addition was small in the case of DSSCs based on **DP-T** (5%), which can be indicative of a good alignment of dye molecules on TiO<sub>2</sub> surfaces. Therefore, the origin of a significantly longer **DP-P** lifetime at even lower dye loads could be ascribed to less tendency for complexation of **DP-P** with oxidizing species in electrolyte. According to a previous finding that polarizability increases the local concentration of oxidizing species in the electrolyte [42], polarizability was calculated for isolated dye molecules. As a result, **DP-P** (65.7 Å<sup>3</sup>) showed less polarity relative to that of **DP-T** (68.0 Å<sup>3</sup>), which might impart **DP-P** an increased  $\tau$ .

#### 3.4. Photovoltaic performance of DSSCs based on DP-T and DP-P

Photovoltaic parameters measured under simulated AM 1.5 G irradiation are listed in Table 1. Four devices were employed which differed in the additives used during cell fabrication. For reference device A without additives, DP-P showed lower current densities  $(5.85 \text{ mA cm}^{-2})$  with respect to **DP-T**  $(8.19 \text{ mA cm}^{-2})$ . IPCE (incident photon to current conversion efficiency) reflected this relative trend in current densities where absorption band edge of the device based on **DP-T** extended to 700 nm. On the other hand, the IPCE spectrum of the device sensitized with DP-P reached ~650 nm for optimized **device A** and **device B** (Fig. 7). These action spectra correlated well with absorption spectra recorded in solution in which DP-T showed both bathochromism and hypochromism relative to DP-P. Bearing in mind that IPCE is defined by a product of LHE( $\lambda$ ),  $\Phi_{ini}(\lambda)$ , and  $\Phi_{c}(\lambda)$  where LHE( $\lambda$ ),  $\Phi_{ini}(\lambda)$ , and  $\Phi_{\rm c}(\lambda)$  means light harvesting efficiency, quantum yield of electron injection, and collection efficiency of injected electrons, respectively [43]. For the present DSSCs based on **DP-T** and **DP-P**, quantum efficiencies were not high despite the presence of driving forces for

Table 1	l					
DSSCs	performance	based (	on dyes	DP-T	and DP-P	a

Dye		$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	$V_{\rm oc}$ [V]	ff	η [%]
DP-T	Device A	8.19	0.618	0.697	3.53
	Device B	8.21	0.618	0.696	3.53
	Device C	6.09	0.700	0.668	2.85
	Device D	6.77	0.691	0.749	3.50
DP-P	Device A	5.85	0.664	0.738	2.86
	Device B	6.08	0.655	0.761	3.03
	Device C	4.55	0.718	0.724	2.37
	Device D	4.53	0.736	0.776	2.59

<sup>a</sup> Photovoltaic parameters were obtained under AM 1.5 G irradiation (100 mW cm<sup>-2</sup>). All devices contained electrolyte composition of 0.6 M DMPII/ 0.1 M LiI/0.05 M I<sub>2</sub> + 0.3 mM dye; **Device B** contained 1 mM DCA as an additive; **Device C** contained 0.5 M TBP and 1 mM DCA as additives.

electron injection followed by dye regeneration. This suggests that either the spectral properties of dye sensitizers were insufficient for high light harvesting efficiency [44] or that alignment of dyes anchored toward the TiO<sub>2</sub> surface negatively affected electron transfer yield defined as  $\Phi_{inj}(\lambda) \cdot \Phi_c(\lambda)$  [45]. From the comparison of current densities of **device B** (containing co-adsorbate DCA) and device A, it was evident that DP-P showed a higher current density (6.08 mA cm<sup>-2</sup>) while **DP-T** reflected a slight increase  $(8.21 \text{ mA cm}^{-2})$ . Considering the ability of DCA to suppress dye aggregation, a lower tendency for **DP-T** aggregate formation on TiO<sub>2</sub> could be responsible for the slight J<sub>sc</sub> increase compared to **DP-P** in device B. On the other hand, device C having TBP as an additive afforded a loss of current density at the expense of driving force for electron injection. Current losses were more significant for DP-T because of its lower LUMO, giving rise to the reduced energy gap between  $E_{cb}$  and  $E_{lumo}$  of the dye. Regarding the open-circuit voltage  $(V_{oc})$  for reference **device** A, the device based on **DP-P** showed 664 mV which is 46 mV higher than that of the device based on **DP-T**. Assuming the  $E_{cb}$  of TiO<sub>2</sub> as -0.5 V versus NHE for all cases, it was found that a significantly increased electron lifetime of the DSSC with sensitizer employing the N-methyl pyrrole spacer seems to contribute to enhancement of  $V_{oc}$  for **DP-P**. Also, compared to device A, enhanced V<sub>oc</sub> for device C was ascribed to the increased  $\tau$  by the addition of TBP. These results clearly show that the passivation effect of TBP [40], which contributes to a  $V_{\rm oc}$ increase. Nonetheless, increased Voc did not compensate for large decrease in current densities, resulting in the lower  $\eta$  compared to reference device A. Device D fabricated with both DCA and TBP gave efficiencies essentially between those from devices B and C. Interestingly, the  $V_{oc}$  of DSSC based on **DP-P** was increased to 736 mV in the presence of TBP and DCA. From the photovoltaic performances of the four types of devices containing the present



**Fig. 7.** IPCE plots for DSSCs sensitized with **DP-P** (a) and **DP-T** (b)\*. \* Denotes: All devices contained electrolyte composition of 0.6 M DMPII/0.1 M Lil/0.05 M I<sub>2</sub> + 0.3 mM dye; **Device B** contained 1 mM DCA as an additive; **Device C** contained 0.5 M TBP as an additive; **Device D** contained 0.5 M TBP and 1 mM DCA as additives.

metal-free sensitizers, it appears that DCA addition can be used to optimize devices exhibiting small  $V_{\rm oc}$  changes by increasing current densities.

#### 4. Conclusions

New D $-\pi$ -A dye sensitizers having either *N*-methyl pyrrole or thiophene  $\pi$ -spacers were synthesized and incorporated into DSSCs. Results from experimental and molecular modeling studies unveiled generic issues for sensitizers arising from the use of these heterocyclic spacers. The DSSC device based *N*-methyl pyrrole (**DP**-**P**) showed good kinetic properties, resulting in high  $V_{0c}$  and making the pyrrole unit a logical spacer for further molecular design studies toward high efficiency DSSCs. Given the similar maximum quantum efficiency (from IPCE data) of the device based on DP-P compared to **DP-T**, an enhanced absorption spectral shift would give high current densities needed for large solar energy capture. It should be added that molecular engineering of sensitizers having an *N*-methyl pyrrole unit should be careful to reduce the dihedral angle between spacers and neighboring group. Such experiments should be augmented by molecular modeling studies designed to examine the behavior of dye sensitizers on TiO<sub>2</sub> in the presence of additives.

#### Appendix A. Supplementary material

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.dyepig.2012.09.001.

#### References

- Grätzel M. Dye-sensitized solar cells. J Photochem Photobiol C 2003;4(2): 145–53.
- [2] Sayama K, Hara K, Mori N, Satsuki M, Suga S, Tsukagoshi S, et al. Photosensitization of a porous TiO electrode with merocyanine dyes containing a carboxyl group and a long alkyl chain. Chem Commun 2000;(13):1173–4.
- [3] Hara K, Kurashige M, Ito S, Shinpo A, Suga S, Sayama K, et al. Novel polyene dyes for highly efficient dye-sensitized solar cells. Chem Commun 2003;(2): 252–3.
- [4] Kitamura T, Ikeda M, Shigaki K, Inoue T, Anderson NA, Ai X, et al. Phenylconjugated oligoene sensitizers for TiO<sub>2</sub> solar cells. Chem Mater 2004;16(9): 1806–12.
- [5] Hara K, Kurashige M, Dan-oh Y, Kasada C, Shinpo A, Suga S, et al. Design of new coumarin dyes having thiophene moieties for highly efficient organicdye-sensitized solar cells. New J Chem 2003;27(5):783–5.
- [6] Hara K, Wang Z-S, Sato T, Furube A, Katoh R, Sugihara H, et al. Oligothiophenecontaining coumarin dyes for efficient dye-sensitized solar cells. J Phys Chem B 2005;109(32):15476–82.
- [7] Schmidt-Mende L, Bach U, Humphry-Baker R, Horiuchi T, Miura H, Ito S, et al. Organic dye for highly efficient solid-state dye-sensitized solar cells. Adv Mater 2005;17(7):813–5.
- [8] Ito S, Miura H, Uchida S, Takata M, Sumioka K, Liska P, et al. High-conversionefficiency organic dye-sensitized solar cells with a novel indoline dye. Chem Commun 2008;(41):5194–6.
- [9] Hwang S, Lee JH, Park C, Lee H, Kim C, Park C, et al. A highly efficient organic sensitizer for dye-sensitized solar cells. Chem Commun 2007;(46):4887–9.
- [10] Ma X, Hua J, Wu W, Jin Y, Meng F, Zhan W, et al. A high-efficiency cyanine dye for dye-sensitized solar cells. Tetrahedron 2008;64(2):345–50.
- [11] Zeng W, Cao Y, Bai Y, Wang Y, Shi Y, Zhang M, et al. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. Chem Mater 2010;22(5): 1915–25.
- [12] Hagberg DP, Yum J-H, Lee H, De Angelis F, Marinado T, Karlsson KM, et al. Molecular engineering of organic sensitizers for dye-sensitized solar cell applications. J Am Chem Soc 2008;130(19):6259–66.
- [13] Ning Z, Zhang Q, Wu W, Pei H, Liu B, Tian H. Starburst triarylamine based dyes for efficient dye-sensitized solar cells. J Org Chem 2008;73(10):3791–7.
- [14] Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, et al. Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells. J Org Chem 2007;72(25):9550–6.
- [15] Chen R, Yang X, Tian H, Sun L. Tetrahydroquinoline dyes with different spacers for organic dye-sensitized solar cells. J Photochem Photobiol A 2007; 189(2–3):295–300.

- [16] Li S-L, Jiang K-J, Shao K-F, Yang L-M. Novel organic dyes for efficient dyesensitized solar cells. Chem Commun 2006;(26):2792-4.
- [17] Jung I, Lee JK, Song KH, Song K, Kang SO, Ko J. Synthesis and photovoltaic properties of efficient organic dyes containing the benzo[b]furan moiety for solar cells. J Org Chem 2007;72(10):3652–8.
- [18] Shen P, Liu X, Jiang S, Wang L, Yi L, Ye D, et al. Synthesis of new N,N-diphenylhydrazone dyes for solar cells: effects of thiophene-derived π-conjugated bridge. Dyes Pigment 2012;92(3):1042–51.
- [19] Shen P, Liu X, Jiang S, Huang Y, Yi L, Zhao B, et al. Effects of aromatic  $\pi$ conjugated bridges on optical and photovoltaic properties of N,Ndiphenylhydrazone-based metal-free organic dyes. Org Electron 2011; 12(12):1992–2002.
- [20] Marinado T, Nonomura K, Nissfolk J, Karlsson MK, Hagberg DP, Sun L, et al. How the nature of triphenylamine-polyene dyes in dye-sensitized solar cells affects the open-circuit voltage and electron lifetimes. Langmuir 2009;26(4): 2592–8.
- [21] Liang Y, Peng B, Chen J. Correlating dye adsorption behavior with the opencircuit voltage of triphenylamine-based dye-sensitized solar cells. J Phys Chem C 2010;114(24):10992-8.
- [22] Bruice PY. Organic chemistry. 3rd ed. Upper Saddle River, N.J.: Prentice Hall; 2001.
- [23] Kim BH. Molecular engineered sensitizers containing heterocyclic spacers in a D $-\pi$ -A system and their use in DSSCs [PhD thesis]: North Carolina State University; 2012.
- [24] Frish MJ. Gaussian 03, revision B.05. Wallingford; 2004.
- [25] Hagfeldt A, Graetzel M. Light-induced redox reactions in nanocrystalline systems. Chem Rev 1995;95(1):49–68.
- [26] Li JJ, Corey EJ. Name reactions in heterocyclic chemistry. Hoboken, N.J.: Wiley-Interscience; 2005.
- [27] Kakushima M, Hamel P, Frenette R, Rokach J. Regioselective synthesis of acylpyrroles. J Org Chem 1983;48(19):3214–9.
- [28] Yang BH, Buchwald SL. Palladium-catalyzed amination of aryl halides and sulfonates. J Organomet Chem 1999;576(1-2):125-46.
- [29] Joule JA, Mills K. Heterocyclic chemistry. Malden, MA: Blackwell Science; 2000.
- [30] Jedrzejewska B, Kabatc J, Pietrzak M, Paczkowski V. Hemicyanine dyes: synthesis, structure and photophysical properties. Dyes Pigment 2003;58(1): 47–58.
- [31] Bard AJ, Faulkner LR. Electrochemical methods: fundamentals and applications. 2nd ed. New York: Wiley; 2001.
- [32] Wiberg J, Marinado T, Hagberg DP, Sun L, Hagfeldt A, Albinsson B. Effect of anchoring group on electron injection and recombination dynamics in organic dye-sensitized solar cells. J Phys Chem C 2009;113(9):3881–6.
- [33] Becker W. Advanced time-correlated single photon counting techniques. Berlin; New York: Springer; 2005.
- [34] DAS6 Fluorescence-decay analysis software user's guide, J81119 ver. E: Horiba Scientific.
- [35] Ghosh HN, Asbury JB, Lian T. Direct observation of ultrafast electron injection from Coumarin 343 to TiO<sub>2</sub> nanoparticles by femtosecond infrared spectroscopy. J Phys Chem B 1998;102(34):6482–6.
- [36] Wiberg J, Marinado T, Hagberg DP, Sun L, Hagfeldt A, Albinsson B. Distance and driving force dependencies of electron injection and recombination dynamics in organic dye-sensitized solar cells. J Phys Chem B 2010;114(45): 14358–63.
- [37] Kamat PV. Photochemistry on nonreactive and reactive (semiconductor) surfaces. Chem Rev 1993;93(1):267–300.
- [38] Chen R, Zhao G, Yang X, Jiang X, Liu J, Tian H, et al. Photoinduced intramolecular charge-transfer state in thiophene-π-conjugated donor–acceptor molecules. J Mol Struct 2008;876(1–3):102–9.
- [39] Ren X, Feng Q, Zhou G, Huang C-H, Wang Z-S. Effect of cations in coadsorbate on charge recombination and conduction band edge movement in dyesensitized solar cells. J Phys Chem C 2010;114(15):7190-5.
- [40] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Mueller E, Liska P, et al. Conversion of light to electricity by cis-X<sub>2</sub>bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. J Am Chem Soc 1993;115(14): 6382–90.
- [41] Lu M, Liang M, Han H-Y, Sun Z, Xue S. Organic dyes incorporating bishexapropyltruxeneamino moiety for efficient dye-sensitized solar cells. J Phys Chem C 2011;115(1):274–81.
- [42] Koops SE, Barnes PRF, O'Regan BC, Durrant JR. Kinetic competition in a coumarin dye-sensitized solar cell: injection and recombination limitations upon device performance. J Phys Chem C 2010;114(17):8054-61.
- [43] Kalyanasundaram K, Grätzel M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. Coord Chem Rev 1998;177(1):347–414.
- [44] Zhang J, Li H-B, Sun S-L, Geng Y, Wu Y, Su Z-M. Density functional theory characterization and design of high-performance diarylamine-fluorene dyes with different [small pi] spacers for dye-sensitized solar cells. J Mater Chem 2012;22(2):568-76.
- [45] Sayama K, Tsukagoshi S, Mori T, Hara K, Ohga Y, Shinpou A, et al. Efficient sensitization of nanocrystalline TiO<sub>2</sub> films with cyanine and merocyanine organic dyes. Sol Energy Mater Sol Cells 2003;80(1):47–71.