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# Novel organic dyes incorporating a carbazole or dendritic 3,6-diiodocarbazole unit for efficient dye-sensitized solar cells



PIGMENTS

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#### 1. Introduction

#### ABSTRACT

Four organic photosensitizers incorporating a carbazole or 3,6-diiodocarbazole unit as the electron donor, a benzene/thiophene or oligothiophene moiety as the conjugated spacer, and 2-cyanoacrylic acid as the electron acceptor have been synthesized. The photovoltaic performance data are quite sensitive to the structural modification of sensitizer. The introduction of the benzene/thiophene linker benefits from lower tendency to aggregate, but disfavors the electron transport between donor and acceptor. The addition of a thiophene unit in the bridge efficiently red-shifts the absorption response, however, organic dyes have some  $\pi$ – $\pi$  aggregation. Incorporation of 3,6-diiodocarbazole as a dendritic donor unit not only enhances the molar extinction coefficients of the absorption but also suppresses the charge recombination with electrolyte.

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Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO<sub>2</sub> have attracted significant attention as low-cost photovoltaic devices due to their high conversion efficiencies over 11% in standard air mass 1.5 and good stability [1]. In these cells as one of the key components ruthenium dyes are used as light absorbers. But the high cost of ruthenium, the necessity of purification treatments, and the low molar extinction coefficients make the research on alternative, metal-free organic dyes appealing for their application in large DSSC modules [2]. Organic photosensitizers have the advantage of high extinction coefficients in the visible region [3]. Also, the position and intensity of the charge transfer transition in organic dyes can be tuned by simple structural modifications such as variation of donor strength and nature of the conjugation pathway [3b]. Therefore, enormous progress has been made in this field, and several organic photosensitizers based on coumarin [4],

indoline [5], and triphenvlamine [6] derivatives have been developed as promising candidates with the power conversion efficiency closing to ruthenium dyes [3b,7]. Although organic photosensitizers exhibit excellent spectral properties, they tend to form aggregates on the semiconductor surface, resulting in self-quenching of the dye excited stated. Another disadvantages of organic photosensitizers are low long-term stability and easy interfacial recombination dynamics, thus leading to low open-circuit photovoltage. Many efforts have been made to design efficient organic photosensitizers through structural modifications in order to prevent the aggregation of dyes and to diminish the charge recombination between the electrons on TiO<sub>2</sub> film and acceptors [3b,8]. A successful approach was achieved by introducing more donor segments to the primary donor, thereby forming donor-donor- $\pi$ bridge-acceptor (D-D- $\pi$ -A) structures. Compared with the D- $\pi$ -A structure constructed by extending  $\pi$ -conjugated bonding bridges, D-D- $\pi$ -A dyes benefit from lower tendency to aggregate and better thermo-stability, and meanwhile their absorption regions can be extended and molar extinction coefficients can be enhanced. Tian et al. has reported a series of D-D- $\pi$ -A structural organic dyes incorporating several donor groups into the triphenylamine framework with starburst configuration, resulting in the red-shift

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in absorption and the suppression of charge recombination with electrolyte [9].

In this work, we report a novel class of organic photosensitizers, containing carbazole or carbazole dendrimer donors and cyanoacrylic acid acceptors (**DX1–DX4**). They are linked via a  $\pi$ -bridge constituted by benzene/thiophene or oligothiophene. Carbazole is a common heterocyclic compound with interesting photo- and electro-chemistries [10], and it is known as an OPC [11] (organic photo conductor) or a hole-transporting material [12]. The incorporation of hole-conductors of carbazole moieties into organic dyes as electron donors have been proved to exhibit supersensitized effects by retarding interfacial charge-recombination dynamics and thus achieving long-lived photoinduced charge separation [13]. Moreover, the dendritic carbazole, which has a rigid and highly twisted starburst structure, shows unique functions in several devices or systems that involve electron transfer [14]. Use of the dendritic carbazole donor could be not only beneficial to high molar extinction coefficients of the absorption but also helps to suppress dark current upon appropriate incorporation of D-D- $\pi$ -A structure. We therefore set out to synthesize a novel dye (DX4) consisting of a 3,6-Diiodocarbazole donor, a 2-cyanoacrylic acid acceptor, and an oligothiophene spacer at the first time. With these dyes as the photosensitizers, we fabricated corresponding DSSCs, and found that the electro-optical properties of **DX4** relative with DX1-3 show significant improvements which manifests in the overall efficiency for the DSSCs.

#### 2. Experimental section

### 2.1. General methods

All reagents were obtained from commercial sources and used as received. Tetrahydrofuran (THF), methylbenzene (MB) and chloroform (CHCl<sub>3</sub>) was purified using MBRAUN MB SPS-800 system. Other solvents were dried over sodium or calcium hydrides and distilled before used. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Mercury-Plus 300FT-NMR spectrometer in DMSO-d<sub>6</sub> or CDCl<sub>3</sub>, respectively. IR spectra were obtained on a Thermo Scientific Nicolet 330 infrared spectrophotometer. MS data were obtained using an LCQ DECA XP liquid chromatographymass spectrometry. UV-vis absorption spectra were measured using a Shimadzu UV-2450 spectrometer. Emission spectra were measured using Shimadzu RF-5301PC spectrometer. Cyclic voltammograms (CV) were recorded using a CHI 832 electrochemical analyzer with FTO/TiO<sub>2</sub>/Dye as working electrode, Ag/AgCl as reference electrode, Pt wire as counter electrode. CVs were measured with 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub>. Scan rate was kept as 50 mV s<sup>-1</sup> for all compounds. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of triarylamine organic dyes obtained from the theoretical calculations were coupled with the redox potential obtained from the CV measurements as shown in main text. 4a [14] and 4c [15] were synthesized according to



(i) Cu, K<sub>2</sub>CO<sub>3</sub>, 18-Crown-6, 1,2-dichlorobenzene; (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, NaCO<sub>3</sub>, THF+H<sub>2</sub>O;
(iii) piperidine, CHCl <sub>3</sub>+CH<sub>3</sub>CN; (iv) KI , KIO<sub>3</sub> , HAc; (v) DMAP, acetone (vi) CuI, K<sub>3</sub>PO<sub>4</sub>, dioxane; (vii) TFA, water, anisole and toluene.

Scheme 1. Synthesis of carbazole -based dyes DX1, DX2, DX3, and DX4.

reported literature. **1-3a**, **1b**, **4b**, and **DX1–4** were prepared according to the procedures listed in the Supporting Information.

## 2.2. Preparation of TiO<sub>2</sub> electrode

The  $TiO_2$  electrode was prepared according to the reported literature procedure [16].

# 2.3. Fabrication of DSSCs

TiO<sub>2</sub> films with 15 µm in thickness were prepared by following the literature procedure [17] and soaked in 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C, which improved the photocurrent and photovoltaic performance of DSSCs. After 30 min, the TiO<sub>2</sub> films were washed with water and ethanol and then sintered at 520 °C for 30 min. After cooling to 80 °C, the TiCl<sub>4</sub> treated TiO<sub>2</sub> electrodes were immersed into 0.3 mM CH<sub>2</sub>Cl<sub>2</sub> solution of the organic dye and kept at room temperature for 16 h. The active area of the dyecoated TiO<sub>2</sub> film was 0.16 cm<sup>2</sup>, which was measured by profilometer (AMBIOS, XP-1). The dye-sensitized TiO<sub>2</sub>/FTO films were sandwiched together with Pt coated FTO glass which was used as a counter electrode. Platinized counter electrodes were fabricated by thermal deposition of H<sub>2</sub>PtCl<sub>6</sub> solution (5 mM in isopropanol) onto FTO glass at 400 °C for 15 min. The electrolyte was injected into the space between the sandwiched cells.

# 2.4. Dye loading measurements

The dye loading measurements on  $TiO_2$  films were carried out by desorbing the dye into 0.8 mol/L triethylamine solution in CH<sub>2</sub>Cl<sub>2</sub> and then measuring the ultraviolet–visible absorption spectra of the resultant solution with the same dilution. The adsorbed density of each dye was calculated from the difference concentration of each solution before and after TiO<sub>2</sub> film immersion.

#### 2.5. Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measurements were performed with a Zennium electrochemical workstation (ZAH-NER) with the frequency range from 10 mHz to 1000 kHz. The magnitude of the alternative signal was 10 mV. The impedance measurements were carried out under forward bias of -0.65 V in the dark.

# 2.6. Characterization of DSSCs

The current–voltage characteristics were measured by using a Keithley 2400 source meter under simulated AM 1.5 G one sun (100 mW cm<sup>-2</sup>) illumination provided by solar simulator (91192, 1 kW Xe lamp with optical filter, Oriel). The electrolyte solution is composed of 0.6 M PMII, 0.03 M I<sub>2</sub>, 0.05 M Lil, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4-tertbutylpyridine (TBP) in acetonitrile and valeronitrile (85:15 v/v).

# 2.7. Computational methods

The geometry structures of four dyes are optimized by means of TD-DFT methods with MO62X functional at 6-311+g(2d,2p) basis set level.

# 3. Results and discussion

# 3.1. Synthesis and structural characterization

The synthetic approach of **DX1**–**4** is outlined in Scheme 1. As for **DX1**, **1a** was synthesized by an Ullman-type condensation of



**Fig. 1.** (a) The absorption spectra of **DX1**, **DX2**, **DX3**, and **DX4** in CH<sub>2</sub>Cl<sub>2</sub> solution. (b) The Absorption spectrum of photosensitizers **DX1**, **DX2**, **DX3**, and **DX4** on TiO<sub>2</sub> nano-crystalline films.

carbazole and excess amount of 1,4-diiodobenzene in the presence of Cu powder as a catalyst and K<sub>2</sub>CO<sub>3</sub>. Then, **1b** was synthesized by using the palladium-catalyzed Suzuki coupling reaction. The final step to obtain DX1 was a Knoevenagel condensation with cyanoacetic acid to convert carbaldehydes to cyanoacrylic acids. The dyes DX2-3 were conveniently obtained from carbazole in three steps involving a suitable phase transfer catalyzed N-alkylation, Suzuki reaction to liberate the aldehyde, and Knoevenagel condensation with cyanoacetic acid. The 3,6-Diiodocarbazole based organic dye DX4 was synthesized in six steps. First, 9-Boc-3,6-diiodocarbazole (I<sub>2</sub>BocCz) was prepared by the iodination of the carbazole followed by Boc protection of the amine group. Next, I2BocCz and the carbazole were reacted by the N-arylation reaction, and then the mixture was deprotected with a mixture of toluene, trifluoroacetic acid (TFA), water, and anisole to produce 4a. Then, 4b was synthesized using Suzuki coupling reaction, and finally DX4 was obtained by Knoevenagel condensation.

# 3.2. Photophysical properties

The absorption spectra of the dyes in  $CH_2Cl_2$  solution are displayed in Fig. 1(a), and the corresponding data are presented in Table 1. All the dyes possess two major prominent peaks at around 290 and >400 nm. The band in the ultraviolet region is probably originating from the electronic transitions localized within the carbazole or starburst carbazole segment. The absorption occurring in the visible region is of charge transfer character, which is sensitive to the nature of the conjugation pathway and red-shifts on progressive addition of thiophene units. The extinction coefficients

Dye	$\epsilon/10^4~M^{-1}~cm^{-1}$ $(\lambda_{max}/nm)$	E <sub>ox</sub> /V (vs Ag/AgCl)	E <sub>ox</sub> /V (vs Fc/Fc <sup>+</sup> ) <sup>a</sup>	$E_{0-0}/\mathrm{eV}^\mathrm{b}$	E <sub>HOMO</sub> /eV (vs vacuum) <sup>c</sup>	E <sub>LUMO</sub> /eV (vs vacuum) <sup>d</sup>	Amounts/10 <sup>-6</sup> mol cm <sup>-2</sup>
DX1	0.87 (416)	1.37	0.74	2.56	-5.54	-2.98	1.43
DX2	0.87 (440)	1.43	0.80	2.38	-5.60	-3.22	1.14
DX3	1.73 (467)	1.28	0.65	2.29	-5.45	-3.16	1.10
DX4	3.46 (465)	1.30	0.67	2.30	-5.47	-3.17	0.53

 Table 1

 Absorption and electrochemical data of the dyes.

 $^{\rm a}$  Oxidation potential of dyes was measured with a scan rate of 50 mV s $^{-1}$  (vs NHE).

<sup>b</sup>  $E_{0-0}$  was determined from the intersection of absorption and emission spectra in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>c</sup>  $E_{\text{HOMO}} [\text{eV}] = -(E_{\text{ox}} (\text{vs Fc/Fc}^+) + 4.8).$ 

<sup>d</sup>  $E_{\text{LUMO}} [eV] = E_{\text{HOMO}} + E_{0-0}.$ 

of all the absorption band of **DX4** with starburst carbazole donor is largest among the four dyes, which is the result of the increase of the number of carbazole units and the conjugation length. The greater maximum absorption coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation. In addition, the dye **DX3** bearing terthiophene as linker shows a significant red-shift and enhancement in extinction coefficient in the longer-wavelength band when compared with that of the dyes **DX1** and **DX2**. Also, the peak position of the charge transfer transition for **DX1** is much shorter when compared with the other three dyes, probably due to the electron-deficiency of the benzene linker relative to the thiophene unit [18].

All the dyes when adsorbed on  $TiO_2$  exhibits red-shifted and broadened absorption profile (Fig. 1(b)) in comparison to that measured in solution, which could be attributed to the aggregation or electronic coupling of the dyes on the  $TiO_2$  surface [9f,19]. In addition, the amount of the dyes adsorbed on the  $TiO_2$  surface is shown in Table 1. The dye loading amounts of for **DX4** is lower than that for **DX1–3**, which may be caused by its cone-shaped molecular configuration. For **DX4**, the starburst carbazole donors can expand the molecular size and lead to the smallest amount of adsorbed dyes on the photoelectrode.

#### 3.3. Electrochemical properties

To evaluate the possibility of electron transfer from the excited dye molecule to the conduction band of TiO<sub>2</sub>, the cyclic voltammograms (CV) of three photosensitizers were measured (Fig. S1) in CH<sub>2</sub>Cl<sub>2</sub> solution, using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. All the dyes demonstrate quasi-reversible redox waves at a moderately high oxidation potential. As seen from Table 1, the first oxidation potentials of all four dyes are more positive than the  $I^-/I_3^-$  redox couple, providing a thermodynamic driving force for efficient dye regeneration. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) derived from the oxidation potentials and absorption/emission data (Fig. S2) of four organic dyes are summarized in Table 1 [20]. Judging from the LUMO values, the excited-state energy levels of three dyes are



Fig. 2. Computed frontier molecular orbitals and electronic distribution in the dyes.



Fig. 3. The IPCE spectra for DSSCs based on four dyes.

much higher than the bottom of the conduction band of TiO<sub>2</sub>, indicating that the electron injection process from the excited dye molecule to TiO<sub>2</sub> conduction band is energetically favorable. Noticeably, the HOMO–LUMO gap  $\Delta E$  decreases with the increment of the number of carbazole electro-donors and thiophene groups in the molecule, in qualitative agreement with theoretical computation results, which may favor light harvesting and hence photocurrent generation in DSSCs.

#### 3.4. Molecular orbital calculations

To scrutinize the geometrical and photophysical properties, molecular orbital calculations of **DX1–4**, were carried out using the TD-DFT and B3LYP/3-21G\* program. The thienyl moiety in **DX2–4** is also coplanar with the 2-cyano-acrylic acid acceptor, due to the extended  $\pi$ -bond conjugation (Fig. S3). Such a group leads to a large electronic interaction that may facilitate the charge separation. Different from **DX2**, **DX1** possesses phenyl and thienyl groups as linkers and the angle between both planes is 28.6°, which does not favor the electron transport between donor and acceptor but benefit from lower tendency to aggregate. Interestingly, as for **DX4**, all dihedral angles between the phenyl planes in carbazole based donors are larger than 64.0° (Table S1) and they are all noncoplanar with each other, which can help to inhibit the close  $\pi$ – $\pi$  aggregation effectively between the starburst structures.

The electronic structures of dyes in  $CH_2Cl_2$  solution were also mimicked, which is the solvent used to record the experimental spectra. The electron distribution of the HOMOs and LUMOs of **DX1**, **DX2**, **DX3**, and **DX4** are shown in Fig. 2. Clearly, the HOMOs of these compounds are delocalized over the carbazole  $\pi$  system with the highest electron density located at the nitrogen atoms of the carbazole moiety. It can be seen that the HOMOs in **DX2** are more delocalized than those in **DX1**, due to the better coplanarity in conjugated pathway. The LUMOs are located in the anchoring

Table 2
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	The	performance	parameters	of the	dye-sensitized	solar	cells.
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Dye	$J_{\rm sc}/{\rm mA~cm^{-2}}$	V <sub>oc</sub> /mV	FF	η(%)
DX1	6.17	601	0.74	2.74
DX2	6.70	589	0.74	2.94
DX3	9.98	586	0.74	4.30
DX4	10.65	643	0.71	4.86
N719 <sup>a</sup>	14.94	765	0.69	7.93

<sup>a</sup> N719 was used as the reference and measured under the same experimental conditions.

group through the  $\pi$  bridge constituted by the benzene and/or thiophene moieties. Thus, the HOMO–LUMO excitation induced by light irradiation could move the electron distribution from the carbazole segment to the anchoring unit through the conjugation pathway. Moreover, as depicted in Table S2, for the four dyes, the S1 state mainly consists of mixed transitions, in which the delocalization of electron density from carbazole to carboxylic groups is apparent. This, in combination with the near unity oscillator strength (*f*), confirms the charge transfer ( $\pi$ – $\pi$ \*) type of transition in the first excited state, supporting the aforementioned experimental results. In addition, the computational UV–Vis spectra of them are consistent with their absorption spectra in CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. S4).

## 3.5. Photovoltaic performance of the DSSCs

The incident monochromatic photon-to-current conversion efficiency (IPCE) with a sandwich cell based on **DX1–4** using 0.6 M 1methyl-3-propyl imidazolium iodide (PMII), 0.1 M guanidinium thiocyanate (GuNCS), 0.05 M LiI, 0.03 M I<sub>2</sub>, 0.5 M tert-butylpyridine in a mixture of acetonitrile and valeronitrile(85: 15) as redox electrolyte is shown in Fig. 3. The onset of IPCE for the device of **DX4** was ca. 700 nm. IPCE values higher than 70% were observed in the range of 400–550 nm with a maximum value of 80% at 490 nm for the device based on **DX4**. The action spectrum of a DSSC with **DX3** exceeds 60% in the visible spectral region from 400 to 540 nm, reaching its maximum of 75% at 490 nm. The action spectrum of **DX3** is red-shifted by 50 nm and 100 nm relative to the **DX2** and **DX1**, respectively.

The photoelectrochemical properties of dyes sensitized TiO<sub>2</sub> electrodes under irradiation of Xe lamp (100 mW cm<sup>-2</sup>) are listed in Table 2, and the corresponding photocurrent–voltage curves are shown in Fig. 4. The short-circuit current ( $J_{sc}$ ) and overall yield ( $\eta$ ) for the four dyes lie in the order **DX4** > **DX3** > **DX2** > **DX1**, which is in accordance with their IPCE results. The **DX4**-sensitized device generates the highest conversion efficiency among four photosensitizers, which may be due to its broad and intense photocurrent action spectrum. Of particular importance is a great (the 57 mV) increase in the open-circuit voltage ( $V_{oc}$ ) of the **DX4**-based cell relative to the **DX3**-based cell. The improved  $V_{oc}$  value is because the starburst carbazole structure might be beneficial for retarding the electron transfer from TiO<sub>2</sub> to the oxidized dye or electrolyte, which would increase the electron lifetime and enhance the open-circuit voltage. In addition, although **DX1**-based cell gave the



Fig. 4. Photocurrent density vs voltage for DSSCs based on dyes under AM 1.5 G simulated solar light (100 mW  $\rm cm^{-2}).$ 



Fig. 5. Electrochemical impedance spectra (a-Nyquist plot; b-Bode plot) of DSSC for four dyes.

lowest  $J_{sc}$  and  $\eta$  among the four cells, its  $V_{oc}$  is higher than that of **DX2** and **DX3**-based cells. The enhancement in  $V_{oc}$  could be attributed to their aggregation-resistant nonplanar linkers containing the phenyl and thienyl groups, which can block the approach of the  $I_3^-$  ion to a certain degree.

Electrochemical impedance spectroscopy (EIS) analyses were also performed to elucidate above photovoltaic findings. In the Nyquist plots (Fig. 5(a)) the radius of the middle semicircle reflects the electron recombination resistance. The electron lifetime ( $\tau$ ) values derived from curve fitting are 93.8, 92.1, 87.8, and 94.9 ms for **DX1**, **DX2**, **DX3**, and **DX4**, respectively. The results are consistent with the  $V_{oc}$  values of the devices. The electron lifetime is improved upon incorporation of the starburst carbazole group, i.e.,  $\tau$  (**DX4**) >  $\tau$  (**DX3**). We thus speculate that the starburst hydrophobic group could form a substantial compact sensitizer layer at the surface of the TiO<sub>2</sub> to prevent the approach of the redox couple.

The Bode phase plots shown in Fig. 5(b) likewise support the differences in the electron lifetime for TiO<sub>2</sub> films derivatized with the four dyes. The middle-frequency peaks of the DSSCs based on **DX1** and **DX4** shift to lower frequency relative to that of **DX2** and **DX3**, indicating a shorter recombination lifetime for the latter species. The increase in the recombination lifetime in the TiO<sub>2</sub> film is associated with a pronounced rise in the charge transfer resistance, which depends on the structure of the dyes. Judging from the optimized structures of **DX2** and **DX3** bearing oligothiophene as linkers, the thienyl moieties in the dyes are coplanar with each other, which may facilitate the electron communication. However, these coplanar molecules, especially for **DX3**, are susceptible to



**Fig. 6.** (a) Incident light intensity dependent recombination time constants, (b) incident light intensity dependent transport time constants, and (c) the charge collection efficiency from IMPS and IMVS.

aggregation for the strong dipole–dipole interaction between the extended delocalized  $\pi$ -bonds. Close  $\pi$ – $\pi$  aggregation between molecules can aggravate charge recombination for the triiodide and can easily penetrate through the big interspaces between chromophores, resulting in the decrease of  $V_{\rm oc}$ .

Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) were carried out to further investigate the different photovoltaic behaviors of four dyes. Fig. 6(a) shows recombination time  $(\tau_r)$  of DSSCs based on DX1, DX2, DX3 and DX4 dyes under various incident light intensities. The results indicate that the recombination time of the devices displays a systematic trend  $\mathbf{DX4} > \mathbf{DX1} > \mathbf{DX2} > \mathbf{DX3}$ . consistent with the EIS results described above. On the other hand, the electron transport times  $(\tau_d)$  of DSSCs based on the four dyes increase in the order **DX1** > **DX2** > **DX4** > **DX3** as shown in Fig. 6(b). Compared with **DX3**, **DX4** has a longer  $\tau_d$ . Considering the interaction with the dye and electrolyte, we deduced it could be the reason that DX4 having starburst structure might limit the access to the surface by Li<sup>+</sup> ions which are known to assist the electron diffusion along the TiO<sub>2</sub> network, resulting in a slower photoinjected electron transport to FTO glass. In addition, the charge collection efficiencies ( $\eta_{cc}$ ) determined by IMPS/IMVS through the equation  $\eta_{cc} = 1 - \tau_d / \tau_r$  are shown in Fig. 6(c). The results indicate that the differences of charge collection efficiency among the dyes are very small, being essentially in the range of 0.990-0.998, implying the main factor affecting the IPCEs and overall conversion efficiencies is the LHE and  $\Phi_{inj}$ , in agreement with the above discussion.

The long-term stability of DSSCs is an important requirement for their practical application. Among many factors affecting the stability of DSSCs, the lifetime is an especially critical factor. Koatoh et al. have developed a simple and efficient method to evaluate the stability of dyes by accelerating the dye aging process upon light irradiation on dye-loaded TiO<sub>2</sub> film without redox electrolyte [21]. Grätzel and Zhu et al. have also tested the photostability of their dyes by this method [9d]. Fig. S5 shows the photographs of the samples of DX1, DX2, DX3, and DX4 adsorbed on TiO<sub>2</sub> surfaces before and after 60 min irradiation. No dramatic change in color was observed for the all the samples. Fig. S6 shows the absorption curves of dyes DX1, DX2, DX3, and DX4 with aging upon light irradiation of AM 1.5 light (5, 10, 30, and 60 min). No substantial change in absorbance was observed for **DX3** and **DX4**, indicating they are stable enough according to Koatoh's experience. For DX1 and DX2, the absorbance at 400-500 nm decreased slightly without no any distinct absorption peak shift as a result of light irradiation. Compared with DX1 and DX2, the photo-stability of DX3 and DX4 seems higher, suggesting that delocalization of holes on the oligothiophene moieties of DX3 and DX4 may enhance their intrinsic photo-stability [21,22]. Meanwhile, the peak positions did not change, implying that no photochemical reaction occurred.

According to the above analyses, the device efficiencies described from I-V curves and IPCE values are in the order of **DX4** > **DX3** > **DX2** > **DX1**, and the electron lifetimes obtained in EIS and IMVS measurements show the order of **DX4** > **DX1** > **DX2** > **DX3**. The outcome of **DX4** with the highest cell efficiency may be rationalized by the following reasons: (1) **DX4** has a higher molar absorption coefficient, resulting in better light harvesting; (2) low aggregation of **DX4** improves its electron injection efficiency and  $J_{sc}$ ; (3) the longer electron lifetime of **DX4** leads to a higher  $V_{oc}$ . On the other hand, the somewhat higher cell efficiencies of **DX2** and **DX3** than **DX1** are mainly attributed to the better spectral properties and electron communication, albeit with shorter electron lifetimes.

#### 4. Conclusions

In summary, we have developed a novel class of organic photosensitizers (**DX1–4**), consisting of a carbazole or dendritic carbazole electron donor and a cyanoacrylic acid electron acceptor, connected by benzene/thiophene or oligothiophene units. The photovoltaic performance was shown to be quite sensitive to the substituent on the photosensitizers. Some general performance trends are clearly discerned as follows: i) The introduction of the benzene/thiophene linker in **DX1**, to a degree, prevents the aggregation of dves and diminishes the charge recombination between the electrons on TiO<sub>2</sub> film and acceptors, but it disfavors the electron transport between donor and acceptor, which reduces the spectral response, thus leading to a lowest  $I_{sc}$  and  $\eta$ . ii) Increasing the conjugation length of the  $\pi$ -linkers from **DX2** to **DX3** can extend the absorption cross section and conduct the bathochromic shift, however, DX3 tends to form aggregates on the semiconductor. iii) Incorporation of dendritic carbazole as a donor unit in DX4 not only enhances the molar extinction coefficients of the absorption but also improves the electron lifetime by leading to an effective spatial separation of the charges, which exhibits the highest  $J_{sc}$ ,  $V_{oc}$ , and  $\eta$  among the four dyes. Our studies open avenues for the development of organic dyes featuring dendritic carbazole as electron donors. By appropriate structural modifications, electron-rich dendritic carbazole can be developed, which may serve as an efficient donor.

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.09.025.

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