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# Triphenylamine-based organic dyes containing benzimidazole derivatives for dye-sensitized solar cells

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#### 1. Introduction

#### ABSTRACT

The synthesis and application to dye-sensitized solar cells of two new triphenylamine-based organic dyes containing benzimidazole derivatives as secondary donors together with a simple triphenylamine derived dye for the purpose of comparison is reported. The photophysical and electrochemical properties of the dyes were investigated by UV–vis spectroscopy and cyclic voltammetry. The introduction of benzimidazole derivatives in the phenyl ring of the triphenylamine core increases the molar extinction coefficients and  $\lambda_{max}$  because of the extension of the  $\pi$ -conjugation structures of the dyes. Overall conversion efficiencies of ~2.5% under full sunlight (AM 1.5G, 100 mW cm<sup>-2</sup>) irradiation were obtained for DSSCs based on these new dyes, under the same conditions, the reference dye and ditetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (N719) gave overall conversion efficiencies of 1.23% and 5.61%, respectively. Our findings demonstrate that the introduction of benzimidazole derivatives as secondary donors in triphenylamine-based dye can improve their photovoltaic performance compared to the unsubstituted reference dye in DSSCs.

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Dye-sensitized solar cells (DSSCs) have received more and more attention due to their relatively high power conversion efficiency and low cost alternative to the conventional photovoltaic devices [1,2]. As a key part of DSSCs, the dyes play a significant role for the DSSCs gaining higher  $\eta$  (photoelectric conversion efficiency) and have been actively studied by researchers all over the world. Up to now, DSSCs based on the ruthenium sensitizers have shown very impressive solar-to-electric power conversion efficiencies, reaching 11% under standard AM 1.5G sunlight [3]. However, the manufacturing costs and environmental issues of the ruthenium sensitizers limit their large-scale application. In order to get the cheaper photosensitizers for DSSCs, pure organic dyes are strongly desired because of their superior molar extinction coefficients, simple preparation and purification procedures and lower cost. Recently, coumarin [4], merocyanine [5], indoline [6], polyene [7], hemicyanine [8], triphenylamine [9], fluorene [10], carbazole [11], phenothiazine [12] and tetrathiafulvalene [13] based-organic dyes have been developed and have achieved solar electrical power conversion efficiencies in the range 5-9 %.

Most of the organic dyes applied in DSSCs show the same character with the electron-donor (D) and the electron acceptor (A) linked by a  $\pi$ -conjugation bridge, which is called the D $-\pi$ -A structure [14]. But it is well known that the major factors for low conversion efficiency of DSSCs based on organic dyes are the formation of dye aggregates on the semiconductor surface and the recombination of conduction band electrons with triiodide in the electrolyte [15].

Among the organic dyes, triphenylamine (TPA) and its derivatives as donor units have displayed promising properties in the development of photovoltaic devices [16–18]. Triphenylamine derivatives are often used as the donor because of their chemical stability, stabilized photoexcited state by charge delocalization in the aryl substituents, and prevention of direct charge recombination between  $TiO_2$  and  $I_3$  by the bulky aryl group covering the  $TiO_2$ [19]. So it is predicted that if introducing a secondary electrondonor to TPA part of dye **TPA-1**, which is a possible alternative to retard the interfacial charge-recombination dynamics and to retain efficient light-induced charge separation, may enhance performance of the dyes for DSSCs.



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Based on these studies, the corresponding dye (**TPA-1**) for the purpose of comparison and two new dyes (**TPA-B1** and **TPA-B2**) by introducing the benzimidazole derivatives to the framework of TPA core, in which the cyanoacetic acid act as acceptor groups, were designed, synthesized and applied in DSSCs. The effects of the different secondary donors in those dyes on the optical, electrochemical properties and photovoltaic performances were studied. The corresponding molecular structures of the three dyes and **N719** are shown in Scheme 1.

# 2. Experimental details

## 2.1. Materials and characterization

All solvents and other chemicals were reagent grade and used without further purification. 1,2-phenylenediamine, cyanoacetic acid and triphenylamine were purchased from Astatech. HRMS data were determined with an FTICR-APEX instrument and a micro TOF-Q II instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Brücker AM 500 NMR instrument. Mp data were obtained on X4 melting point detector (FUKA, Beijing, China).

### 2.2. Theoretical calculations

Gaussian 03 package was used for density functional theory (DFT) calculation [20]. The geometries and energies of **TPA-1**, **TPA-B1**, and **TPA-B2** were determined using the B3LYP method with the 6-31G (d) basis set. None of the frequency calculations generated negative frequencies, being consistent with an energy minimum for the optimized geometry.

## 2.3. Photophysical and electrochemical measurements

INSPECT F Scanning electron microscopy (SEM) (FEI, Netherlands) is used to measure the thickness of the film. Absorption spectra were measured with SHIMADZU (model UV1700) UV–vis spectrophotometer. FT-IR spectra were obtained

on Nicolet 6700. Cyclic voltammetry experiments were performed on a CH Instruments 660C electrochemical workstation at a scan rate of 50 mV/s in dimethylformamide (DMF) ( $5.0 \times 10^{-4}$  M) containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, platinum as counter and work electrodes and Ag/AgCl as reference electrode.

### 2.4. Synthesis

Compounds **1** [21], **2** [22], 5,6-diaminobenzo[d] [1,3]dithiole-2thione [23] and **TPA-1** [21] were prepared according to the reported literature (as shown in Scheme 2).

#### 2.4.1. Compound 3

A methanol (20 mL) solution of 1,2-phenylenediamine (108 mg, 0.10 mmol), compound **2** (300 mg, 0.10 mmol) were charged sequentially in a three-necked flask and heated under reflux for 3 h. After cooling to room temperature, solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with dichloromethane/ethyl acetate (10:1, v:v) as eluent to afford compound **3** as a yellow solid (105 mg, yield 26%). Mp 163–166 °C. FT-IR (KBr, cm<sup>-1</sup>): 3059, 1690, 1588, 1491, 1163. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 12.87(s, 1H), 9.82 (s, 1H), 8.16–8.18 (d, *J* = 8.4 Hz, 2H), 7.78–7.80 (d, *J* = 8.4 Hz, 2H), 7.44–7.52 (m, 3H), 7.19–7.30 (m, 8H), 7.04–7.06 (d, *J* = 8.8 Hz, 2H). HRMS (*m*/*z*): calcd for C<sub>26</sub>H<sub>19</sub>N<sub>3</sub>O: 389.1528, found 390.1590 [M + H]<sup>+</sup>.

#### 2.4.2. Compound 4

A methanol (20 mL) solution of 5,6-diaminobenzo[d] [1,3] dithiole-2-thione (213 mg, 0.10 mmol), compound **2** (300 mg, 0.10 mmol) were charged sequentially in a three-necked flask and heated under reflux for 12 h. After cooling to room temperature, solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with dichloromethane/ethyl acetate (6:1, v:v) as eluent to afford compound **4** as a deep yellow solid (109 mg, yield 22%). Mp 186–189 °C. FT-IR (KBr, cm<sup>-1</sup>): 1688, 1589, 1487, 1063. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 13.30$  (s, 1H), 9.84 (s, 1H), 8.18–8.21 (d, J = 8.4 Hz, 2H), 8.12 (s,

**OTBA** 



Scheme 1. Molecular structures of TPA-1, N719, TPA-B1 and TPA-B2.



Scheme 2. Synthetic routes of the dyes TPA-1, TPA-B1 and TPA-B2. (a) POCl<sub>3</sub>, DMF, 1,2-dichloroethane, reflux, 12 h; (b) POCl<sub>3</sub>, DMF, chloroform, reflux, 72 h (c) 1,2-phenylenediamine, methanol, reflux, 3 h (d) 5,6-diaminobenzo[d] [1,3]dithiole-2-thione, methanol, reflux, 10 h (e) 2-cyanoacetic acid, piperidine, acetonitrile, reflux.

2H), 7.79–7.82 (d, J = 8.4 Hz, 2H), 7.45–7.48 (t, J = 15.6 Hz, 2H), 7.28–7.30 (d, J = 8.8 Hz, 3H), 7.23–7.24 (d, J = 7.2 Hz, 2H), 7.07–7.09 (d, J = 8.8 Hz, 2H). HRMS (m/z): calcd for C<sub>27</sub>H<sub>17</sub>N<sub>3</sub>OS<sub>3</sub>:495.0534, found 496.0591[M + H]<sup>+</sup>.

#### 2.4.3. TPA-B1

A CH<sub>3</sub>CN (15 mL) solution of compound **3** (80 mg, 0.2 mmol), cyanoacetic acid (57 mg, 0.67 mmol) and a few drops of piperidine were charged sequentially in a three-necked flask and heated to reflux for 5 h. After cooling to room temperature, solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with dichloromethane/ethanol (1:1, v:v) as eluent to afford the dye TPA-B1 as a yellow solid (45 mg, yield 49%). Mp 233–236 °C. FT-IR (KBr, cm<sup>-1</sup>): 2219, 1694, 1577, 1496, 1186. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 8.21-8.23$  (d, *J* = 8.8 Hz, 2H), 8.17 (s, 1H), 7.96–7.99 (d, *J* = 8.8 Hz, 2H), 7.58–7.60 (m, 2H), 7.45–7.49 (t, J = 15.6 Hz, 2H), 7.29–7.31 (d, J = 8.8 Hz, 2H), 7.25-7.27 (d, J = 7.6 Hz, 2H), 7.19-7.21 (m, 2H), 7.03-7.05 (d, J = 9.2 Hz, 2H). <sup>13</sup>C NMR  $\delta$  (400 MHz, DMSO- $d_6$ ):  $\delta = 165.65, 163.99,$ 152.89, 151.09, 150.68, 146.78, 145.12, 132.77, 130.19, 128.04, 126.62, 126.14, 125.91, 125.24, 124.08, 122.04, 119.93, 116.99, 115.70. HRMS-EI(m/z): calcd for C<sub>29</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> : 456.1586, found 456.1581 [M]<sup>+</sup>. UV–vis (ethanol, nm):  $\lambda_{max}$  (molar extinction coefficient) = 421 (48,000).

## 2.4.4. TPA-B2

A procedure is similar to that for the dye **TPA-B1** but with compound **4** (70 mg, 0.14 mmol) instead of compound **3**. The deep yellow solid (38 mg, yield 48%) is **TPA-B2**. Mp 256–258 °C. FT-IR (KBr, cm<sup>-1</sup>): 2217, 1585, 1488, 1329, 1065. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.38 (s, 1H), 8.22 (s, 1H), 8.19–8.20 (d, *J* = 3.6 Hz, 2H), 8.11 (s, 2H), 7.97–8.0 (d, *J* = 8.8 Hz, 2H), 7.45–7.49 (t, *J* = 15.6 Hz, 2H), 7.28–7.32 (m, 3H), 7.24–7.26 (d, *J* = 7.2 Hz, 2H), 7.04–7.07 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 213.51, 163.93, 153.21, 151.03, 147.47, 145.05, 144.61, 132.83,

130.23, 128.42, 126.70, 126.04, 125.10, 124.98, 124.27, 120.29, 116.81. HRMS (*m/z*): calcd for C<sub>30</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: 562.0592, found 563.0673 [M + H]<sup>+</sup>. UV–vis (ethanol, nm):  $\lambda_{max}$  (molar extinction coefficient) = 410 (74,900).

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

TiO<sub>2</sub> colloid was prepared according to the literature [24]. The washed FTO glass substrates were immersed in 40 mM TiCl<sub>4</sub> aq. at 70 °C for 30 min to form a compact layer of TiO<sub>2</sub>, which plays an important role in suppressing the charge recombination of DSSCs at the interface between FTO and electrolyte, then washed with water and ethanol. A thin film of TiO<sub>2</sub> was prepared on the FTO substrate with the compact TiO<sub>2</sub> layer through blade coating with glass rod. After drying the nanocrystalline TiO<sub>2</sub> layer at 80 °C, the TiO<sub>2</sub> thin film with more layers was achieved by repeating the blade coating above process two times. Finally TiO2 electrodes were treated at 450 °C for 30 min. After cooling to room temperature, the electrodes were immersed in 40 mM TiCl<sub>4</sub> ag. at 70 °C for 30 min, and washed with water and ethanol again, then recalcined at 450 °C for 30 min. After the sintering, when the TiO<sub>2</sub> electrodes cooled to 80 °C, the electrodes were immersed in a dye bath containing 0.2 mM TPA-1, TPA-B1, TPA-B2 and N719 in ethanol and left overnight. The films were then rinsed in ethanol to remove excess dye. In our experiment, open cells were fabricated in air by clamping the different dyed electrode with platinized counter electrode. The electrolyte used here composed of 0.6 M 1,2dimethyl-3-propylimidazolium iodide (DMPII), 0.0653 M LiI, 0.03 M I<sub>2</sub>, 0.28 M 4-tertbutylpyridine (TBP) and 0.05 M guanidium thiocyanate (GuSCN) in acetonitrile.

#### 2.6. Photovoltaic characterization

The irradiation source for the photocurrent action spectrum measurement is a photosource (CHF-XM-500W, Trusttech Co. Ltd.,

Beijing, China) with a CH Instruments 660C electrochemical workstation (Shanghai CH Instruments Co., China). The incident light intensity was 100 mW cm<sup>-2</sup> calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of  $0.4 \text{ cm}^2$ . The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). Electrochemical impedance spectroscopy (EIS) data were obtained in the dark under forward bias 0.7 V, scanning from  $10^{-2}$  to  $10^5$  Hz with ac amplitude of 10 mV by using CH Instruments 660C electrochemical workstation.

# 3. Results and discussion

## 3.1. Optical properties

As the function of light harvesting, the dye plays a significant role for the DSSCs achieving high conversion efficiency and the absorption spectra of the dye could affect the device performance dramatically [25]. The UV-vis spectra of the dyes TPA-1, TPA-B1 and TPA-B2 in ethanol solution were measured (Fig. 1) and the characteristic data are collected in Table 1. The absorbance  $\lambda_{max}$  at 421 nm of **TPA-B1** is red-shift 11 nm compared with the  $\lambda_{max}$  at 410 nm of TPA-1. And the molar extinction coefficient of TPA-B1 is 48,000 M<sup>-1</sup> cm<sup>-1</sup>, which is higher than that of **TPA-1**. The change of the molar extinction coefficients of TPA-B1 and TPA-B2 is possible owing to introducing benzimidazole derivatives to the framework of TPA core. Although the maxima absorption peak of **TPA-B2** has not red-shift compared with that of TPA-1, the molar extinction coefficient (74,900  $M^{-1}$  cm<sup>-1</sup>) of **TPA-B2** is much higher than that of **TPA-1** (40,700  $M^{-1}$  cm<sup>-1</sup>) and the maxima absorption spectra are generally broadened. This indicates that introducing benzimidazole derivatives to the framework of TPA core resulting in **TPA-B2** with an improved light harvesting ability.

Fig. 2 shows the absorption spectra of **TPA-1**, **TPA-B1** and **TPA-B2** on 6.94  $\mu$ m thick TiO<sub>2</sub> films after 12 h immersion. The maximal absorption peaks for **TPA-1**, **TPA-B1** and **TPA-B2** on the TiO<sub>2</sub> films are located at 443 nm, 449 nm and 464 nm, respectively. The absorption spectra are generally broadened and red-shifted as compared to the dyes dissolved in ethanol, implying that most of the dyes were adsorbed on the TiO<sub>2</sub> surface with only partial J-type aggregates [26]. The broadening and red-shifting of absorption spectra are beneficial for light harvesting of the solar spectrum.



Fig. 1. Absorption spectra of TPA-1, TPA-B1 and TPA-B2 recorded in ethanol.

Table 1	
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U	V-	-vis	and	e	lectroc	hem	ical	d	ata.
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Dye	$\lambda_{\max}^{a/nm}$ ( $\epsilon^{b}/M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\max}^{c}/nm$	E <sub>ox</sub> <sup>d</sup> /V (vs. NHE)	$E_{g}^{e}/eV$	E <sub>ox*</sub> <sup>f</sup> /V (vs. NHE)
TPA-1	410 (40,700)	443	1.03	2.10	-1.07
TPA-B1	421 (48,000)	449	1.27	2.08	-0.81
TPA-B2	410 (74,900)	464	1.32	2.02	-0.70

<sup>a</sup> Absorption is measured in ethanol solution (1.0 × 10<sup>-5</sup> M) at room temperature. <sup>b</sup> The molar extinction coefficient at  $\lambda_{max}$  of the absorption spectra.

<sup>c</sup> Absorption spectra of the dyes adsorbed on TiO<sub>2</sub> electrodes.

<sup>d</sup>  $E_{\rm ox}$  was measured in DMF with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte (scanning rate: 50 mV s<sup>-1</sup>, working electrode and counter electrode: Pt wires, and reference electrode: Ag/AgCl), potentials measured vs Ag/AgCl were converted to normal hydrogen electrode (NHE) by addition of +0.2 V.

 $^{\rm e}~E_{\rm g}$  was estimated from the absorption spectra of  $\rm TiO_2$  electrodes sensitized by the dyes.

 $E_{ox^*}$  was calculated from  $E_{ox} - E_{g}$ .

Based on the Tauc relation, the energy gap  $(E_g)$  can be obtained by plotting  $(ahv)^2$  vs. hv and extrapolating the linear portion of  $(ahv)^2$  to zero as shown in Fig. 3 [27]. The  $E_g$  of **TPA-1**, **TPA-B1** and **TPA-B2** are estimated to be 2.10 eV, 2.08 eV and 2.02 eV, respectively. The red-shift of **TPA-B1** and **TPA-B2** adhering to TiO<sub>2</sub> thin films can be evidenced by the lower energy band-gap as compared with that of **TPA-1**.

### 3.2. Electrochemical properties

The energetic alignment of the HOMO and LUMO energy levels is crucial for an efficient operation of the dye in DSSCs. To ensure efficient electron injection from the excited dye into the conduction band of TiO<sub>2</sub>, the LUMO level must be higher in energy than the TiO<sub>2</sub> conduction band edge. The HOMO level of the dye must be lower in energy than the redox potential of the  $I^-/I_3^-$  redox couple for efficient regeneration of the dye cation after photoinduced electron injection into the TiO<sub>2</sub> film. Cyclic voltammetry is a preliminary characterization technique to determine the redox properties of organic dyes.

Cyclic voltammetry measurements were performed in dimethylformamide (DMF) solution using 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte (Fig. 4), and the corresponding data are summarized in Table 1. The first oxidation potentials ( $E_{ox}$ ) corresponds to the HOMO levels of the dyes (**TPA-1**: 1.03 V vs NHE; **TPA-B1**: 1.27 V vs NHE; **TPA-B2**: 1.32 V vs NHE) are



Fig. 2. Absorption spectra of TiO<sub>2</sub> films sensitized by TPA-1, TPA-B1 and TPA-B2.



**Fig. 3.** Plot of  $(ahv)^2$  vs. hv.

more positive than the  $I^-/I_3^-$  redox potential (0.4 V vs NHE), which indicates that the oxidized dyes formed from respective electron injection into the conduction band of TiO<sub>2</sub> will favorably accept electrons from I<sup>-</sup> ions thermodynamically. This could lead to a fast dye-regeneration, avoiding the charge recombination between oxidized dyes and photoinjected electrons in the nanocrystalline TiO<sub>2</sub> film. The excited state oxidation potentials ( $E_{ox}^+$ ) of the dyes can be obtained by the first oxidation potentials ( $E_{ox}^+$ ) of the dyes can be obtained by the first oxidation potentials ( $E_{ox}^+$ ) and the energy gaps ( $E_g$ ) of the dyes, namely,  $E_{ox} - E_g$ . The  $E_{ox}^+$  of the **TPA-1**, **TPA-B1** and **TPA-B2** are -1.07, -0.81 and -0.70 V vs. NHE, respectively. The  $E_{ox}^+$  of the dyes are more negative than the band edge energy of the nanocrystalline TiO<sub>2</sub> electrode (-0.5 V vs NHE) [28], indicating that the electron injection process from the excited dye molecule to TiO<sub>2</sub> conduction band is energetically permitted. The schematic energy levels of **TPA-1**, **TPA-B1** and **TPA-B2** based on absorption and electrochemical data are shown in Fig. 5.

#### 3.3. Theoretical calculations

To get further insight into the effect of molecular structure and electron distribution of **TPA-1**, **TPA-B1** and **TPA-B2** on the



Fig. 4. Cyclic voltammograms of TPA-1, TPA-B1 and TPA-B2 in DMF.



Fig. 5. Schematic energy levels of TPA-1, TPA-B1 and TPA-B2 based on absorption and electrochemical data.

performances of dye-sensitized solar cells, their geometries and energies were optimized by density functional theory (DFT) calculation at the B3LYP/6-31G(d) level with Gaussian 03 [20].

The ground-state geometries of the three dyes are shown in Fig. 6, and the optimized geometries indicate that the three benzene rings in the triphenylamine cores are non-planar, which could reduce contact between molecules and enhance their thermo-stability [29].

Fig. 7 shows the frontier orbital plots of the HOMOs and LUMOs of **TPA-1**, **TPA-B1** and **TPA-B2**. The HOMOs of **TPA-1**, **TPA-B1** and **TPA-B2** dyes are delocalized in large extent over the donor parts and the bridge, indicating that the binding energy of the electrons in the HOMOs is sensitive to the change in the  $\pi$ -system [30]. Illumination produces an excited state (LUMOs) in these dyes, and intramolecular charge transfer occurs, resulting in the electron movement from the donor groups to the acceptor groups. The electron densities of the secondary electron-donors (the benz-imidazole derivatives) in the LUMOs of **TPA-B1** and **TPA-B2** are very low. This indicates that both of the secondary electron-donors in the framework of TPA core could enhance the photo-generated charge separation under light illumination compared with that of **TPA-1**.

## 3.4. Photovoltaic properties

The incident photon-to-current conversion efficiencies (IPCE) of the DSSCs based on **TPA-1**, **TPA-B1** and **TPA-B2** are measured in the visible region (300–800 nm), as shown in Fig. 8. The highest IPCE values of 53% at 430 nm for **TPA-B1** and 51% at 420 nm for **TPA-B2** are much higher than 23% at 410 nm for **TPA-1**, which might be attributable to the higher molar extinction coefficient of **TPA-B1** and **TPA-B2**. It can be seen clearly that the photocurrent response of **TPA-B1** and **TPA-B2**-sensitized DSSCs is much better than that of **TPA-1** in the range of 375–525 nm, which implies the dyes would show a relatively larger photocurrent in DSSCs. On the other hand, the IPCE values for **TPA-1**, **TPA-B1** and **TPA-B2** obviously decrease after 500 nm, which can be attributed to the decrease of light harvesting properties.

Fig. 9 shows the current–voltage characteristics of dyesensitized solar cells employing with **TPA-1**, **TPA-B1**, **TPA-B2** and **N719** as sensitizers under a photosource with the light intensity as 100 mW cm<sup>-2</sup>. The detailed photovoltaic parameters are summarized in Table 2, where **TPA-1** and **N719** are included for comparison. The **TPA-B1-**sensitized solar cell gave a short-circuit



Fig. 6. Optimized geometries of TPA-1, TPA-B1 and TPA-B2.

photocurrent density ( $J_{sc}$ ) of 5.12 mA cm<sup>-2</sup>, an open-circuit voltage ( $V_{oc}$ ) of 0.659 V, and a fill factor (ff) of 0.72, corresponding to an overall conversion efficiency of 2.43% (see Table 2). The **TPA-B2**-sensitized solar cell gave a  $J_{sc}$  of 6.12 mA cm<sup>-2</sup>, a  $V_{oc}$  of 0.679 V, and a ff of 0.64, corresponding to an overall conversion efficiency of 2.65%.

According to Fig. 9 and Table 2, it is clear that the photovoltaic performances of the DSSCs can be evidently affected by introducing a benzimidazole unit and a substituted benzimidaole unit into the formwork of TPA core. In comparison with **TPA-1**, both the  $J_{sc}$  and  $V_{oc}$  values of **TPA-B1** and **TPA-B2** are improved by introducing secondary donor to TPA part. **TPA-B1** and **TPA-B2** have a higher  $J_{sc}$  which might be due to the secondary donors increasing the ability of TPA core's electron-donating potential. It can be deduced from the higher molar extinction coefficient and IPCE of **TPA-B1** and **TPA-B2** than that of **TPA-1**. The higher  $V_{oc}$  of **TPA-B1** and **TPA-B2** than that of **TPA-1** might be due to the comparatively lower  $E_{ox}$ 

(HOMO) than that of the **TPA-1**, which offers a significantly larger driving force for the reduction of the oxidized dye. This, in turn, will lead to a slower back electron transfer from TiO<sub>2</sub> to the dye and result in a lager  $V_{oc}$  value [31]. The higher  $J_{sc}$  and  $V_{oc}$  for the DSSCs of **TPA-B1** and **TPA-B2** lead to the higher efficiencies than that of **TPA-1**, and increases in  $\eta$  of about 97% and 115% were obtained from **TPA-1** to **TPA-B1** and **TPA-B2**, respectively.

Electrochemical impedance spectroscopy (EIS) is a useful tool for characterizing important interfacial charge transfer processes in DSSCs, such as the charge recombination at the  $TiO_2/dye/electro-lyte$  interface, electron transport in the  $TiO_2$  electrode, electron transfer at the counter electrode, and  $I_3^-$  transport in the electrolyte. In this study, impedance spectra of the solar cells based on **TPA-1**, **TPA-B1** and **TPA-B2** were performed to further elucidate the photovoltaic properties.

Fig. 10 shows the EIS Nyquist plots for DSSCs based on **TPA-1**, **TPA-B1** and **TPA-B2**. The DSSCs were measured in the dark under



Fig. 7. The electron distribution of the HOMOs and LUMOs of TPA-1, TPA-B1 and TPA-B2.



Fig. 8. The IPCE spectra of the DSSCs sensitized with TPA-1, TPA-B1 and TPA-B2.



Fig. 9. Current density-voltage curves of DSSCs based on TPA-1, TPA-B1, TPA-B2 and N719.

forward bias (0.70 V) for the frequency ranging from 0.01 Hz to 100 kHz. With the bias voltage applied, the larger semicircle at lower frequencies corresponded to the charge-recombination processes at the TiO<sub>2</sub>/dye/electrolyte interface. As shown in Fig. 8, the radius of the semicircle in the intermediate frequency regime of the Nyquist plot is in the order of **TPA-B2** > **TPA-B1** > **TPA-1**, indicating that the recombination rate is increased in the order of **TPA-B2** < **TPA-B1** < **TPA-1** in the dark [32]. This trend appears to be consistent with the  $V_{oc}$  values of **TPA-B2** (0.679 V), **TPA-B1** (0.659 V) and **TPA-1** (0.640 V), which is reasonable to conclude that the better performance of **TPA-B1**, **TPA-B2** can be ascribed to a reduced rate of charge recombination leading to higher values of  $V_{oc}$  compared with that of **TPA-1**.

Table 2 Photovoltaic performances of DSSCs based on TPA-1, TPA-B1, TPA-B2 and N719.

Dye	$J_{\rm sc}/{\rm mA~cm^{-2}}$	V <sub>oc</sub> /V	ff	η%
TPA-1	3.16	0.640	0.61	1.23
TPA-B1	5.12	0.659	0.72	2.43
TPA-B2	6.12	0.679	0.64	2.65
N719	11.56	0.714	0.68	5.61



Fig. 10. Impedance spectra measured in the dark under forward bias (0.70 V) with TPA-1, TPA-B1 and TPA-B2.

## 4. Conclusions

In summary, two new triphenylamine-based organic dyes (TPA-B1 and TPA-B2) containing benzimidazole derivatives as secondary donors were designed, synthesized and applied in dye-sensitized solar cells. The corresponding dye TPA-1 was prepared for the purpose of comparison. The effects of introducing benzimidazole derivatives as secondary donors into the formwork of TPA core on the optical, electrochemical, and photovoltaic properties were studied. Density functional theory calculation shows that both of the secondary electron-donors in the framework of TPA core could enhance the photo-generated charge separation under light illumination compared with that of TPA-1. The overall conversion efficiencies of 2.43%  $(J_{\rm sc} = 5.12 \ {
m mA} \ {
m cm}^{-2}, \ V_{\rm oc} = 0.659 \ {
m V}, \ ff = 0.72)$  and 2.65%  $(J_{\rm sc} = 6.12 \text{ mA cm}^{-2}, V_{\rm oc} = 0.679 \text{ V}, ff = 0.64)$  were obtained for DSSCs based on TPA-B1 and TPA-B2, respectively. In comparing with **TPA-1** ( $\eta = 1.23\%$ ,  $J_{sc} = 3.16$  mA cm<sup>-2</sup>,  $V_{oc} = 0.640$  V, ff = 0.64), the photovoltaic performances of **TPA-B1** and **TPA-B2** were significantly improved. The present results strongly suggest that benzimidazole derivatives as secondary donors in triphenvlamine-based dves can strongly improve photovoltaic performances of TPA-B1 and TPA-B2. Further structural optimization, such as broadening the absorption spectra and tuning the energy levels, is very likely to generate more efficient sensitizers and this work is currently underway in our laboratory.

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#### Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2012.05.007.

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