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Influence of the auxiliary acceptor and π -bridge in carbazole dyes on photovoltaic properties



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ABSTRACT

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Keywords: Carbazole sensitizer Benzothiadiazole π-Bridge Synthesis Photovoltaic performance Six *N*-dimethylfluorenylcarbazole dyes have been synthesized based on benzene, furan and thiophene π -bridge with or without benzothiadiazole auxiliary acceptor. Their photophysical properties and photovoltaic performance are investigated systematically based on the incorporation of benzothiadiazole and the variety of π -bridges. The presence of benzothiadiazole broadens the absorption spectra and favors the light-harvesting abilities, which benefits better IPCE spectra and accordingly improved *J*_{SC}. In addition, benzothiadiazole plays a role on the effects of π -bridge on the photoelectrical conversion efficiency. Dye bearing thiophene bridge achieves optimal photovoltaic performance 4.14% among those carbazole dyes without benzothiadiazole while when with benzothiadiazole dye bearing furan bridge exhibits the best cell efficiency 4.96% under AM 1.5G condition (N719 dye's 6.57% under the same condition).

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1. Introduction

Crystalline silicon solar cell is the main representative of the solar energy utilization, which has a mature application technology and high market share [1]. However, the requirement of ultrapure silicon single crystals promotes the improvement of alternative photovoltaic solar cells [2]. Dye-sensitized solar cell (DSSC), a promising environmentally friendly photovoltaic device for converting sunlight to electricity, has aroused a lot of attention due to their low material cost, flexibility, easy manufacturing process and high photovoltaic performance [3].

In DSSC, the light-harvesting ability and electron injection efficiency of dye molecules are the determining factors for the photoelectrical conversion performance. The possibility of improving the photovoltaic performance through small change of the molecular structure raises the diverse design for metal-free organic sensitizers [4–7]. Metal-free organic sensitizer is characterized with high molar extinction coefficient, wide absorptive spectrum and low cost, which help it win the superiority to metal organic sensitizer [8]. A typical structure of metal-free organic sensitizer is composed of an electron donor, a π -bridge and an electron acceptor arranged in a donor- π -bridge-acceptor (D- π -A)

http://dx.doi.org/10.1016/j.jphotochem.2016.08.033 1010-6030/© 2016 Elsevier B.V. All rights reserved. system. Various donors and π -bridges are introduced in the molecular engineering of metal-free organic sensitizers to improve the spectral properties and photovoltaic performance [9–13]. The incorporation of another auxiliary acceptor is also an efficient design concept and D-A- π -A-based sensitizers have witnessed considerable progress in the enhancement of the photovoltaic performance [14]. The presence of another electron-deficient acceptor may not only facilitate intramolecular charge transfer (ICT) thus enhancing the light harvesting ability, but also decrease the energy level of LUMO orbital improving the dye photostability, which contribute to most efficient and stable sensitizers for DSSC application [15]. In 2012, Zhu et al. reported an indoline sensitizer bearing benzothiadiazole acceptor with power conversion efficiency 9.04% [16]; Kim et al. synthesized three triarylamine sensitizers based on thieno[3,2-b][1]benzothiophene unit and found a triarylamine sensitizer with benzothiadiazole-phenyl unit exhibits a better photoelectrical conversion efficiency 10.47% than that with benzothiadiazole- thiophene unit [17].

Among the common used auxiliary acceptor, benzothiadiazole (BTZ) with good electron-withdrawing ability is an extensively exploited acceptor in the design of D-A- π -A sensitizers and outstanding long-term stability is observed in the benzothiadiazole-based D-A- π -A sensitizers [18]. We ever reported D-A- π -A carbazole sensitizers **ZXY-1–ZXY-4** by incorporating benzothia-diazole into carbazole dyes [19]. It is found **ZXY-3** with benzene bridge gives better photoelectrical conversion efficiency than **ZXY**-



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1 with thiophene bridge. In fact, π -bridge is crucial to the photovoltaic performance in the design of new sensitizers, which plays a key role in intramolecular charge transfer. Benzene and five-member heterocycles are the common used π -bridges and usually benzene benefits the photovoltage while furan and thiophene favor the photocurrent [20–23]. The ultimate cell efficiency is determined by the combined effect of π -bridge and the rest of the molecule.

Carbazole and their derivatives are characterized with electron-rich property and good hole-transporting capability, which have been used as electroluminescent, non-linear optical (NLO) and photorefractive materials [24]. In addition, electron-rich and bulky fluorene units [25] are always used in the sensitizers to enhance the electron-donating ability of the donor and suppress the charge recombination. Therefore, in order to further improve the photovoltaic performance and investigate the principle of molecular engineering, we synthesized six *N*-dimethylfluorenylcarbazole dyes based on different aryl bridges with or without benzothiadiazole and investigated the relationship between the structure of carbazole dyes and the photovoltaic performance.

2. Experimental

2.1. Materials and characterization

Nuclear magnetic resonance spectra were recorded on Bruker Avance III 500 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. Mass spectra were measured using a Waters Xevo Q-Tof Mass Spectrometer. Absorption spectra were measured with SHIMADZU (model UV2550) UV–vis spectrophotometer. Fluorescence spectra were obtained on a SHIMADZU RF-5301PC spectrofluorometer.

2.2. Fabrication of DSSCs

The FTO glass was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. For the fabrication of photoelectrodes, titanium nanoxide paste was deposited by screen-printing, resulting in the TiO₂ electrodes. The thickness of TiO₂ film was 12 µm. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min. After being cooled to 80 °C, the TiO₂ electrode was immersed into the dye solution in a mixture of MeOH and CHCl₃ (V_{MeOH}: V_{CHCI3} = 1:10) and kept at room temperature for 24 h to assure complete dye uptake, which were then rinsed with MeOH to remove excess dye. Meanwhile, the counter electrodes were prepared by screen-printing a 50 nm Pt layer on the cleaned FTO plates. Open cells were fabricated in air by clamping the different photoelectrodes with platinized counter electrodes. The electrolyte used here is composed of the CH₃CN solution of 0.3 M 1,2dimethyl-3-propylimidazolium iodide (DMPII), 0.03 M I₂, 0.07 M LiI, 0.1 M guandine thiocyanate, and 0.4 M 4-tert-butylpytiding (TBP). The active area of DSSCs was 0.36 cm².

2.3. Photovoltaic characterization

The photovoltaic performance of the DSSCs was evaluated at AM 1.5 G illumination (100 mW/cm²; Sol3A, Newport, USA) using a Keithley digital source meter (Keithley 2420, USA). The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by a Hypermono-light (SM-25, Jasco, Japan). Electrochemical impedance spectros-copy (EIS) experiments were conducted using a computer-controlled potentiostat (ZeniumZahner, Germany). The measured

frequency ranged from 100 mHz to 1 MHz while the AC amplitude was set to 10 mV. The bias of all EIS measurements was set to the V_{OC} of the corresponding dyes.

2.4. General procedure for the synthesis of compounds

2.4.1. Synthesis of 9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazole **I** To a solution of carbazole (2.00 g, 12 mmol) and 2-bromo-9,9dimethyl-9H-fluorene (2.73 g, 10 mmol) in dry and degassed xylene (60 mL) were added Pd(OAc)₂ (0.07 g, 0.30 mmol), P(t-Bu)₃·HBF₄ (0.29 g, 1.00 mmol), Cs₂CO₃ (9.75 g, 30 mmol). The mixture was refluxed for 15 h under N₂ atmosphere. After the reaction was finished, the mixture was cool down to room temperature and filtered. The filtrate was concentrated to dryness and the residue was purified with silica-gel column chromatography (petroleum) to afford compound **I** as a white solid (3.02 g, 84%), m.p. 123.5–124.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51 (t, *J* = 9 Hz, 3H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 8 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 1.59 (s, 6H).

2.4.2. Synthesis of 3-bromo-9-(9,9-dimethyl-9H-fluoren-2-yl)- 9H-carbazole II

Compound II was synthesized in DMF through the similar method reported by Ref [26] as a white solid (0.43 g, 98%). m.p. 94–96 $^{\circ}$ C.

2.4.3. Synthesis of 3-(7-bromo-2,1,3-benzothiadiazol-4-yl)-9-(9,9dimethyl-9H- fluoren-2-yl)- 9H-carbazole III

The solution of **II** (4 g, 9.12 mmol) in anhydrous THF (50 mL) was cooled to -78 °C, and then n-BuLi (6.84 mL, 10.9 mmol, 1.6 mol/L in hexane) was added dropwisely. The reactant was stirred for 1 h and then trimethyl borate (1.56 mL, 13.68 mmol) was added at once. The mixture was allowed to warm to room temperature and stirred for 20 h. The obtained solution was used directly in the subsequent Suzuki coupling without further treatment.

Under a nitrogen atmosphere, benzothiadiazole(3.0 g, 10.2 mmol), Pd(PPh₃)₄ (1.17 g, 1.02 mmol) and aqueous K₂CO₃ (19 mL, 2 mol/L) were dissolved in THF (60 mL). After the reactant was refluxed for 14 h, the mixture was extracted with CH₂Cl₂ and washed with water. The combined organic layer was dried over NaSO₄, filtered and concentrated. The residue was purified by column chromatography (V_{PE}:V_{EA}=5:1) to give compound **III** as a yellow solid (2.97 g, 50.8%). m.p. 199 ~ 202 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, *J*=1.4 Hz, 1H), 8.26 (d, *J*=7.8 Hz, 1H), 8.01 (dd, *J*=8.6, 1.8 Hz, 1H), 7.99 (d, *J*=7.6 Hz, 1H), 7.97 (d, *J*=8.0 Hz, 1H), 7.84 (dd, *J*=6.5, 1.5 Hz, 1H), 7.72 (d, *J*=7.9, 1.9 Hz, 1H), 7.54-7.47 (m, 3H), 7.45-7.39 (m, 2H), 7.36 (ddd, *J*=7.9, 6.5, 1.6 Hz, 1H), 1.58 (s, 6H)

2.4.4. Synthesis of 5-[7-(9-(9,9-dimethyl-9i-fluoren-2-yl)-9Hcarbazol-3-yl)-2,1,3-benzothiadiazol-4-yl]- 2thiophenecarboxaldehyde **IVa**

A mixture of compound **III** (1.74 g, 3.04 mmol), (5-formylthiophen-2-yl)boronic acid (0.69 g, 4.4 mmol), Pd(PPh₃)₄ (0.35 g, 0.30 mmol), aqueous K₂CO₃ (2 M, 6 mL) in THF (18 mL) was refluxed for 10 h under N₂ atmosphere. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}: V_{PE}=2:1) to afford compound **IVa** as a yellow solid (0.72 g, 40%). m.p. 243– 244 °C; ¹H NMR (500 MHz, CDCl₃) δ : 10.02 (s, 1H), 8.80 (d, *J* = 1.5 Hz, 1H), 8.28-8.27 (m, 2H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.10 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 4.0 Hz, 1H), 7.84 (dd, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.53–7.48 (m, 3H), 7.46–7.40 (m, 2H), 7.40–7.35 (m, 1H), 1.60 (s, 6H).

2.4.5. Synthesis of 2-cyano-3-[5-[7-(9-(9,9-dimethyl-9H-fluoren-2yl)-9H-carbazol-3-yl)-2,1,3-benzothiadiazol-4-yl]-2-thienyl]- 2propenoic acid **LY-S**

To a solution of compound **IVa** (0.2 g, 0.33 mmol) and cvanoacetic acid (0.06 g, 0.7 mmol) in THF (20 mL), piperidine (0.16 mL) was added. The mixture was refluxed for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{CH2CI2}: V_{CH3OH}: V_{HAc}=400: 8: 2) to afford compound **LY-S** as a purple solid (0.18 g, 80%). m.p. 269–271 °C; ¹H NMR (500 MHz, DMSO) δ: 8.99 (s, 1H), 8.57 (s, 1H), 8.44 (d, J = 7.6 Hz, 1H), 8.38 (dd, J = 7.8 Hz, 1H), 8.34 (d, J = 4.1 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 8.17-8.10 (m, 3H), 7.97 (d, J = 7.1 Hz, 1H), 7.94 (s, 1H), 7.65 (t, J=8.8 Hz, 2H), 7.60 (d, J=8.6 Hz, 1H), 7.55-7.48 (m, 2H), 7.45-7.40 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 1.56 (s, 6H); ¹³C NMR (125 MHz, DMSO) δ: 163.58, 155.28, 153.66, 153.09, 151.78, 147.57, 146.27, 140.71, 140.24, 139.62, 139.54, 138.01, 137.73, 136.36, 135.59, 134.24, 128.28, 127.70, 127.56, 127.45, 127.22, 126.54, 125.35, 122.97, 122.93, 122.83 (2C), 121.50, 121.27, 121.18, 121.13, 120.67, 120.35 (2C), 116.50, 109.91, 109.70, 98.64, 46.83, 26.61 (2C); IR v/cm⁻¹ (KBr): 3442.74, 2921.87, 2221.29, 1797.14, 1686.9, 1574.91, 1490.42, 1456.01, 1422.76, 1353.01, 1242.67, 885.43, 811.29, 738.00; HRESIMS *m*/*z* 669.1456 [M-H][–], cacld C₄₁H₂₆N₄O₂S₂ for: 670.1497; Elemental analysis calcd (%): C 73.41, H 3.91, N 8.35; Found (%):C 73.70, H 3.97, N 8.25.

2.4.6. Synthesis of 5-[7-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2,1,3-benzothiadiazol-4-yl]- 2-furancarboxaldehyde **IVb**

A mixture of compound III (0.5 g, 0.875 mmol), (5-formylfuran-(0.245 g,1.75 mmol), 2-vl)boronic acid $Pd(PPh_3)_4$ $(0.1 \, g)$ 0.0875 mmol), aqueous K₂CO₃ (2 M, 1.75 mL) in THF (18 mL) was refluxed for 10 h under N₂. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2} : V_{PE} = 2:1) to afford compound **IVb** as a yellow solid (0.25 g, 49%). m.p. 155–157 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.77 (s, 1H), 8.81 (d, J = 1.6 Hz, 1H), 8.45 (d, J = 7.5 Hz, 1H), 8.29 (d, J = 7.8 Hz, 1H), 8.11 (dd, J = 8.6, 1.8 Hz, 1H), 7.98 (d, J = 5.5 Hz, 1H), 7.97 (d, J = 4.2 Hz, 2H), 7.84 (d, J = 6.6 Hz, 1H), 7.69 (d, J = 1.8 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.60 (dd, J = 7.9, 1.9 Hz, 1H), 7.53-7.51 (m, 2H), 7.50-7.48 (m, 2H), 7.44 -7.41 (m, 2H), 7.39-7.36 (m, 1H), 1.60 (s, 6H).

2.4.7. Synthesis of 2-cyano-3-[5-[7-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2,1,3-benzothiadiazol-4-yl]-2-furanyl]- 2-propenoic acid **LY-F**

To a solution of compound **IVb** (0.2 g, 0.34 mmol) and cyanoacetic acid (0.06 g, 0.7 mmol) in THF (20 mL), piperidine (0.16 mL) was added. The mixture was refluxed for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{CH2CI2}: V_{CH3OH}: V_{HAc}=400: 8: 2) to afford compound LY-F as a purple solid (0.153 g, 69%). m.p. 259- $262 \circ C$; ¹H NMR (500 MHz, DMSO) δ : 9.04 (d, J = 1.6 Hz, 1H), 8.39 (t, J=7.8 Hz, 2H), 8.28 (dd, J=8.7, 1.8 Hz, 1H), 8.24 (d, J=7.6 Hz, 1H), 8.21 (s, 1H), 8.16 (d, J=8.0 Hz, 1H), 7.98 (d, J=3.9 Hz, 2H), 7.95 (d, J=1.9Hz, 1H), 7.70 (d, J=3.7Hz, 1H), 7.67 (dd, J=8.0, 1.9Hz, 1H), 7.64 (d, J=6.7 Hz, 1H), 7.60 (d, J=8.6 Hz, 1H), 7.54-7.49 (m, 2H), 7.45-7.40 (m, 2H), 7.40-7.36 (m, 1H), 1.59 (s, 6H); ¹³C NMR (125 MHz, DMSO) δ:163.70, 155.28, 154.39, 153.66, 153.07, 150.93, 147.44, 140.69, 140.24, 140.22, 138.00, 137.74, 135.60, 134.41, 128.25, 127.67, 127.27, 127.21, 126.50, 126.02, 125.35, 123.01, 122.88(2C), 121.46, 121.39, 121.17, 121.11, 120.70, 120.40, 118.63, 118.59, 116.56, 114.91, 114.85, 109.90, 109.57, 98.39, 46.83, 26.61 (2C); IR ν /cm⁻¹ (KBr): 3451.83, 2925.84, 2222.59, 1696.64, 1605.49, 1544.42, 1462.81, 1424.37, 1348.24, 1231.96, 1028.14, 808.31, 739.88; HRESIMS *m*/*z* 653.1653 [M–H]⁻, cacld C₄₁H₂₆N₄O₃S for: 654.1726; Elemental analysis calcd (%): C 75.21, H 4.00, N 8.56; Found (%): C 75.30, H 4.32, N 8.95.

2.4.8. Synthesis of 4-[7-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9Hcarbazol-3-vl)-2,1,3-benzothiadiazol-4-vl]- benzaldehyde **IVc**

A mixture of compound **III** (0.2 g, 0.35 mmol), (4-formylphenyl) boronic acid (0.11 g, 0.7 mmol), Pd(PPh₃)₄ (0.04 g, 0.035 mmol), aqueous K₂CO₃ (2 M, 0.7 mL) in THF (18 mL) was refluxed for 10 h under N₂ atmosphere. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}: V_{PE} = 2:1) to afford compound **IVc** as a yellow solid (0.13 g, 62%). m.p. 249–252 °C; ¹H NMR (500 MHz, CDCl₃) δ : 10.15 (s, 1H,), 8.79 (d, *J* = 1.5 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 2H), 8.12-8.09 (m, 3H), 7.99 (d, *J* = 2.7 Hz, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.53-7.49 (m, 3H), 7.45-7.41 (m, 2H), 7.39-7.36 (m, 1H), 1.60 (s, 6H,).

2.4.9. Synthesis of 2-cyano-3-[4-[7-(9-(9,9-dimethyl-9H-fluoren-2yl)-9H-carbazol-3-yl)-2,1,3-benzothiadiazol-4-yl]phenyl]- 2propenoic acid **LY-P**

To a solution of compound **IVc** (0.2 g, 0.33 mmol) and cvanoacetic acid (0.06 g, 0.7 mmol) in THF (20 mL), piperidine (0.16 mL) was added. The mixture was refluxed for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{CH2CI2}: V_{CH3OH}: V_{HAc}=400: 8: 2) to afford compound LY-P as a purple solid (0.186 g, 84.5%). m.p. $257 \sim 259 \,^{\circ}\text{C}$; ¹H NMR (500 MHz, DMSO) δ 8.99 (d, $I = 1.6 \,\text{Hz}, 1 \,\text{H}$), 8.42 (s, 1H), 8.39 (d, /=7.7 Hz, 1H), 8.32 (d, /=8.5 Hz, 2H), 8.25 (d, J=8.5 Hz, 2H), 8.22 (dd, J=8.6, 1.7 Hz, 1H), 8.18 (d, J=2.9 Hz, 1H), 8.16 (d, J = 3.5 Hz, 1H), 7.98 (d, J = 6.8 Hz, 1H), 7.96 (d, J = 1.9 Hz, 1H), 7.68 (dd, J = 8.0, 1.9 Hz, 1H), 7.65 (d, J = 6.6 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.56–7.49 (m, 2H), 7.47–7.42 (m, 2H), 7.40 (d, J=7.4Hz, 1H), 7.37 (d, J = 6.5 Hz, 1H), 1.57 (s, 6H); ¹³C NMR (125 MHz, DMSO) δ : 165.36, 163.08, 155.31, 153.64, 153.20, 153.01, 140.94, 140.81, 140.30, 138.04, 137.67, 135.65, 134.03, 130.61 (2C), 129.73, 129.50 (2C), 129.09, 128.70, 127.71, 127.61, 127.11, 126.51, 125.45, 122.98, 122.80, 122.74, 121.45, 121.23, 121.20, 120.61, 120.30, 120.25, 116.24, 115.37, 109.88, 109.72, 104.47, 78.42, 46.78, 26.58; IR ν/cm^{-1} (KBr) 3445.4, 2921.87, 2518.91, 2228.91, 2141.06, 1796.65, 1596.69, 1546.44, 1461.69, 1358.41, 1232.14, 1090.6, 883.73, 734.04; HRESIMS m/z 663.1887 [M-H]⁻, cacld C₄₃H₂₈N₄O₂S for: 664.1933; Elemental analysis calcd (%): C 77.69, H 4.25, N 8.43; Found (%):C 78.05, H 4.45, N 8.05.

2.4.10. Synthesis of 5-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2-thiophenecarboxaldehyde **Va**

A mixture of compound **II** (1.74 g, 4.00 mmol), (5-formylthiophen-2-yl)boronic acid (0.69 g, 4.4 mmol), Pd(PPh₃)₄ (0.46 g, 0.40 mmol), aqueous K₂CO₃ (2 M, 7 mL) in THF (18 mL) was refluxed for 10 h under N₂ atmosphere. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}: V_{PE}=2:1) to afford compound **Va** as a yellow solid (0.59 g, 31%). m.p. 224 ~ 226 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.91 (s, 1H), 8.48 (d, *J* = 1.6 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 3.9 Hz, 1H), 7.77 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.63 (d, *J* = 1.7 Hz, 1H), 7.55-7.51 (m, 2H), 7.50-7.49 (m, 4H), 7.42 (td, *J* = 6.6, 1.1 Hz, 2H), 7.40-7.36 (m, 1H), 1.59 (s, 6H). 2.4.11. Synthesis of 2-cyano-3-[5-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2-thienyl]- 2-propenoic acid **LT-S**

Compound **LT-S** was synthesized through the method reported by Ref [27] as a purple solid (0.22 g, 74%). m.p. 276–278 °C; ¹H NMR (500 MHz, DMSO) δ 13.78 (bs, 1H, COOH), 8.79 (s, 1H), 8.51 (s, 1H), 8.43 (t, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 3.7 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 1H), 7.91 (d, *J* = 6.1 Hz, 2H), 7.86 (d, *J* = 3.8 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.47–7.36 (m, 4H), 1.54 (s, 6H).

2.4.12. Synthesis of 5-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2-furancarboxaldehyde **Vb**

A mixture of compound **II** (1.10 g, 2.5 mmol), (5-formylfuran-2-yl)boronic acid (0.55 g, 3.75 mmol), Pd(PPh₃)₄ (0.29 g, 0.25 mmol), aqueous K₂CO₃ (2 M, 5 mL) in THF (30 mL) was refluxed for 10 h under N₂. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}: V_{PE}=2:1) to afford compound **Vb** as a pink solid (0.6 g, 53%). m.p. 135 ~ 137 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.67 (s, 1H), 8.69 (d, *J* = 1.6 Hz, 1H), 8.25 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J*=8.0 Hz, 1H), 7.89 (dd, *J*=8.6, 1.6 Hz, 1H), 7.83 (d, *J*=10.7, 4.0 Hz,1H), 7.64 (d, *J*=1.8 Hz, 1H), 7.55 (dd, *J*=7.9, 2.0 Hz, 1H), 7.53–7.51 (m, 2H), 7.50–7.47 (m, 2H), 7.45–7.40 (m, 2H), 7.40–7.36 (m, 2H), 6.89 (d, *J*=3.8 Hz, 1H), 1.58 (s, 6H); HRESIMS *m/z* 454.1808 [M+H]⁺, cacld C₃₂H₂₃NO₂ for: 453.1729

2.4.13. Synthesis of 2-cyano-3-[5-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)-2-furanyl]-2-propenoic acid **LT-F**

To a solution of compound **Vb** (0.23 g, 0.50 mmol) and cyanoacetic acid (0.09 g, 1.00 mmol) in THF (20 mL), piperidine (0.19 mL) was added. The mixture was refluxed for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{CH2CI2}: V_{CH3OH}: V_{HAc}=400: 4: 1) to afford compound **LY-F** as a red solid (0.16 g, 62%). m.p. 278 \sim 280 °C; ¹H NMR (500 MHz, DMSO) δ 13.61 (bs, 1H, COOH), 8.87 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.11 (dd, J = 8.0, 3.5 Hz, 1H), 8.08 (d, J = 2.0 Hz, 1H), 8.04 (dd, J = 8.7, 1.7 Hz, 1H), 7.95 (d, J = 6.7 Hz, 1H), 7.91 (t, J = 2.3 Hz, 1H), 7.63-7.60 (m, 3H), 7.54-7.49 (m, 2H), 7.47 (d, J=8.4 Hz, 1H), 7.42–7.38 (m, 4H), 1.53 (s, 6H); ¹³C NMR (125 MHz, DMSO) & 165.66 (2C), 164.16, 160.19, 155.40, 153.71, 147.09, 140.99, 140.89, 138.30, 137.73, 135.27, 127.78, 127.26, 127.16, 127.1, 125.56, 123.59, 123.28, 122.90 (2C), 122.50, 121.63, 121.35, 120.85, 120.50, 115.58 (2C), 110.62, 110.32, 108.76, 95.90, 46.92, 26.63, 24.62; IR ν/cm^{-1} (KBr) 3444.67, 2958.98, 2218.47, 1723.37, 1678.52, 1599.05, 1534.39, 1455.57, 1284.32, 1229.91, 1132.4, 1046.12, 885.86, 805.26, 742.54; HRESIMS m/z 519.1722 [M–H]⁻, cacld C₃₅H₂₄N₂O₃ for: 520.1787; Elemental analysis calcd (%): C 80.75, H 4.65, N 5.38; Found (%):C 81.07, H 5.03, N 5.17.

2.4.14. Synthesis of 4-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9Hcarbazol-3-yl)-benzaldehyde **Vc**

A mixture of compound **II** (1.66 g, 3.79 mmol), (4-formylphenyl) boronic acid (0.66 g, 4.40 mmol), Pd(PPh₃)₄ (0.44 g, 0.38 mmol), aqueous K₂CO₃ (2 M, 7.5 mL) in THF (18 mL) was refluxed for 10 h under N₂ atmosphere. The reaction was quenched with water. The reactant was extracted with dichloromethane and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}: V_{PE}=2:1) to afford compound **Vc** as a yellow solid (0.93 g, 53%). m.p. 200–202 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.10 (s, 1H), 8.46 (d, *J* = 1.6 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.84 (dd, *J* = 6.6, 1.4 Hz, 1H), 7.75 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.42 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.37 (td,

J = 6.1, 3.0 Hz, 1H), 1.59 (s, 6H). HRESIMS m/z 464.2014 [M+H]⁺, cacld C₃₄H₂₅NO for: 463.1936

2.4.15. Synthesis of 2-cyano-3-[4-(9-(9,9-dimethyl-9H-fluoren-2-yl)-9H-carbazol-3-yl)phenyl]- 2-propenoic acid **LT-P**

To a solution of compound Vc (0.93 g, 2.00 mmol) and cyanoacetic acid (0.35 g, 4.00 mmol) in THF (20 mL), piperidine (0.75 mL) was added. The mixture was refluxed for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{CH2CI2} : V_{CH3OH} : V_{HAC} =400: 4: 1) to afford compound **LY-P** as a yellow solid (0.93 g, 88%). m.p. 268–270 °C; ¹H NMR (500 MHz, DMSO) δ 14.0 (bs, 1H, COOH), 8.81 (s, 1H), 8.41 (d, *J* = 8.3 Hz, 2H), 8.20 (d, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *I* = 7.9 Hz, 2H), 7.97–7.92 (m, 3H), 7.63 (d, *I* = 7.1 Hz, 2H), 7.55–7.46 (m, 3H), 7.44–7.35 (m, 3H), 1.55 (s, 6H); ¹³C NMR (125 MHz, DMSO) δ 163.64, 155.38, 153.83, 153.71, 145.21, 140.87, 140.47, 138.11, 137.75, 135.62, 131.52 (2C), 130.53, 129.70, 127.72, 127.24, 127.07 (2C), 126.72, 125.50, 125.38, 123.56, 122.88 (2C), 121.58, 121.30, 120.45 (2C), 120.40, 119.27, 116.42, 110.38, 109.99, 102.51, 46.88, 26.64 (2C); IR v/cm⁻¹ (KBr) 3447.29, 2959.11, 2226.7, 1795.46, 1696.33, 1583.03, 1463.49, 1423.44, 1365.28, 1275.15, 1232.06, 1189.37, 799.35, 738.88; HRESIMS *m*/*z* 529.1923 [M-H]⁻, cacld C₃₇H₂₆N₂O₂ for: 530.1994; Elemental analysis calcd (%): C 83.75, H 4.94, N 5.28; Found (%):C 83.36, H 4.78, N 4.92.

3. Results and discussion

3.1. Synthesis

The synthetic pathway of carbazole dyes is depicted in Scheme 1. *N*-(dimethylfluorenyl)carbazole I was synthesized through the substitution reaction of carbazole on N atom by 2-bromo-9,9-dimethyl-9*H*-fluorene under the catalysis of Pd(OAc)₂. The bromide II, obtained through the bromination of I with NBS, reacted with formylarylboronic acids through Suzuki coupling reaction to give the intermediate aldehydes V. LT-series dyes were synthesized through the condensation of V with cyanoacetic acid. Bromide II was coupled with 4,7-dibromobenzothiadiazole to form the intermediate III. The second Suzuki coupling was occurred between III and formylarylboronic acids to afford the aldehydes IV. IV reacted with cyanoacetic acid to produce LY-series dyes.

3.2. Optical properties

The UV-vis spectra of the carbazole dyes in CHCl₃-CH₃OH solution are displayed in Fig. 1(a) and (b), and the corresponding data are summarized in Table 1. LT-series dyes exhibit two absorption peaks: one peak at about 310 nm is ascribed to $\pi \rightarrow \pi^*$ transition and the other peak is found at 350-400 nm caused by intramolecular charge transfer from the carbazole donor to the cyanoacrylic acid acceptor through π -bridge (Fig. 1(a)). After the introduction of benzothiadiazole, ICT absorption peaks of LY-series dyes shift bathochromically about 100 nm when compared with LT-series dyes and the responsive wavelength of LY-series dyes is extended to 550-600 nm from 500 nm of LT-series dyes (Fig. 1(e)). Moreover, an additional peak between the $\pi \rightarrow \pi^*$ and ICT absorption peak is observed at 350-400 nm which benefits blue light harvesting of LY-series dyes. Therefore, the incorporation of BTZ facilitates the efficient ICT and expands the light absorption region, improving the light-harvesting capabilities of LY-series dyes.

On the other hand, in these carbazole dyes, the incorporation of the electron-rich furan or thiophene bridge leads to the bath-ochromic shift of λ_{max} by ${\sim}40\,\text{nm}$ along with the distinct broadening of the absorption spectra when compared with dyes bearing benzene bridge. Replacement of furan with thiophene has



Scheme 1. Syntheses of carbazole dyes.

little effect on λ_{max} but leads to the improvement of the molar extinction coefficient and the expansion of the absorption spectra. Compared with **LT-F, LT-S** has higher molar extinction coefficients for $\pi \to \pi^*$ transition peak and ICT peak. However, the incorporation of BTZ closes the gap and the molar extinction coefficients of three peaks for **LY-S** are similar with those of **LY-F**.

Fig. 1(c) and (d) list the absorption spectra of carbazole dyes on TiO₂ film. Dyes bond with TiO₂ through the deprotonation of the carboxylic acid anchoring group and form the aggregates on TiO₂ film. The deprotonation of the carboxylic acid to form the carboxylate-TiO₂ unit with reduced electron-withdrawing ability weakens ICT, which leads to the blue shift of λ_{max} combining with H-aggregates. Instead of parallel arrangement of H-aggregates, Jaggregates with head to tail arrangement usually induce the absorption peak shift bathochromically. As can be seen, these carbazole dyes exhibit broader absorption spectra by 50 nm on TiO₂ film than in solution due to the formation of aggregates. Red shift of λ_{max} for LT-series dyes is observed indicating the formation of J-aggregates. Among LT-series dyes, LT-S exhibits the best absorption spectrum on TiO₂ film indicating the best light harvesting ability and LT-F has broader absorption spectrum than LT-P though with lower absorbance. The incorporation of BTZ leads to the broadening of the absorption spectra region of LY-series dyes (Fig. 1(f)). Interestingly, contrary to LT-series dyes, LY-series dyes exhibit blue shift of λ_{max} on TiO₂ film compared with in solution, which may be caused by the deprontonation of the carboxylic acid group and the parallel arrangement of dyes on TiO₂ film. Moreover, **LY-F** instead of **LY-S** shows the broadest absorption spectrum with the highest absorbance intensity among LY-series dyes and exhibits superior light harvesting ability.

3.3. Computational analysis

To gain insight of the relationship between the structure and the photophysical properties, the ground state geometries of carbazole dyes have been optimized by the B3LYP hybrid density functional method in conjunction with the *d*-polarized 6-31G (d) basis set implemented in the Gaussian 03 program.

The optimized structures of carbazole dyes were listed in Fig. 2. As can be seen, **LT-P** and **LY-P** with six-member benzene ring as π -bridge exhibit weak planarity and the dihedral angles of benzene with carbazole and benzothiadiazole unit are 34° and 35°, respectively. With the replacement of benzene ring with five-member thiophene or furan ring, the dihedral angle between



Fig. 1. UV-vis absorption spectra of carbazole dyes. (a) LT-series dyes in CHCl₃-CH₃OH solution (V_{CHCl3} : V_{CH3OH} = 10:1); (b) LY-series dyes in CHCl₃-CH₃OH solution (V_{CHCl3} : V_{CH3OH} = 10:1); (c) LT-series dyes on TiO₂ film; (d) LY-series dyes on TiO₂ film; (e) six carbazole dyes in CHCl₃-CH₃OH solution (V_{CHCl3} : V_{CH3OH} = 10:1); (f) six carbazole dyes on TiO₂ film; (e) six carbazole dyes in CHCl₃-CH₃OH solution (V_{CHCl3} : V_{CH3OH} = 10:1); (f) six carbazole dyes on TiO₂ film.

 π -bridge and carbazole or benzothiadiazole unit decreases and good planarity is observed. This is in good accordance with longer maximum absorption wavelength of the dyes with thiophene or furan π -bridge. The incorporation of benzothiadiazole brings about a dihedral angle of about 35° between carbazole and benzothiadiazole unit, and LY-series dyes exhibit inferior planarity to LT-series dyes. However, compared with LT-series dyes, LY-series dyes exhibit the bathochromical shift of λ_{max} due to their low energy gap derived from the electron-withdrawing property of benzothiadiazole as shown in Fig. 3, which counteracts their inferior planarity.

Fig. 3 shows the energy gaps of LT-series dyes are located at -3.0 to -2.94 eV while those of LY-series dyes are found at -2.60 to -2.50 eV, indicating the energy modulating ability of

Tab	le 1

Electrooptical parameters of carbazole dyes.

Compd.	λ_{\max}^{a} /(nm)	ϵ^{a} /(M ⁻¹ cm ⁻¹)	λ_{max}^{b} /(nm)	λ_{em}^{c} /(nm)	HOMO ^d /(eV)	LUMO ^d /(eV)	E _{gap} d /(eV)
LT-P	306, 350	38467, 40400	389	495	-5.46	-2.46	3.0
LT-F	305, 390	21433, 24167	404	480	-5.31	-2.37	2.94
LT-S	316, 392	27367, 35967	411	500	-5.43	-2.48	2.95
LY-P	324, 351, 443	41900, 24033, 22833	431	565	-5.12	-2.51	2.61
LY-F	323,401, 489	26833, 14266, 23967	469	596	-5.05	-2.56	2.49
LY-S	322,401, 489	24533, 13366, 24633	463	601	-5.11	-2.55	2.56

^a Maximum absorption wavelength λ_{max} and molar extinction coefficient at λ_{max} of dyes measured in CHCl₃-CH₃OH solution.

^b Maximum absorption wavelength λ_{max} of dyes on sensitized TiO₂ electrodes.

^c Maximum emission wavelength measured in CHCl₃-CH₃OH solution.

^d Calculated at the B3LYP/6-31G* level in vacuum.



Fig. 2. Optimized geometries (side view) of carbazole dyes at the B3LYP/6-31G(d) level.



Fig. 3. The energy level of the frontier molecular orbitals of carbazole dyes at B3LYP/6-31G(d), including HOMO-2 (olive), HOMO-1 (blue), HOMO (navy), LUMO (red), LUMO+1 (magenta) and LUMO+2 (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

benzothiadiazole. The calculated energy gaps of these carbazole dyes basically agree with the λ_{max} as shown in Table 1 and large λ_{max} relates to small energy gap. **LT-P** and **LY-P** with benzene π -bridge exhibit small λ_{max} and larger energy gap than those with furan or thiophene π -bridge. Compared with LT-series dyes, the incorporation of benzothiadiazole raises the HOMO energy level of LY-series dyes by 0.3 eV, while the LUMO energy level of LY-series dyes have been shifted downwards by 0.05–0.19 eV. Both the increase of the HOMO energy level and the decrease of the LUMO energy level contribute to the narrowing energy gap of LY-series dyes corresponding to their bathochromic λ_{max} .

Fig. 4 lists the electron distribution in the frontier molecular orbital HOMO and LUMO. LY-series dyes have similar electron distribution with LT-series dyes. The HOMOs delocalized over the whole molecules for dyes with thiophene or furan π -bridge. In the case of **LT-P** and **LY-P** with benzene bridge, their HOMOs are mainly composed by the donor and the donor along with the auxiliary acceptor, respectively, perhaps resulting from the large dihedral between benzene and carbazole or benzothiadiazole. Since the LUMOs are mostly populated on the whole molecule except the donor, the LUMOs have a good overlap with the HOMOs favoring the efficient electron excitation and injection into the conduction band of TiO₂.



Fig. 4. Frontier molecular orbitals of carbazole dyes.

3.4. Electrochemical properties

Electrochemical impedance spectroscopy (EIS) is used to investigate electron recombination of DSSCs based on carbazole dyes and conducted in the dark under the bias of V_{OC} . The corresponding Nyquist and Bode spectra are listed in Fig. 5 along with the equivalent circuit. The corresponding resistance parameters were obtained through software ZSimpWin and listed in Table 2. In the equivalent circuit, R_S refers to the overall series resistance and the similar R_S (about 28–37 Ω) of these carbazole

Table 2

Parameters obtained by fitting the impedance spectra of DSSCs based on carbazole dyes using equivalent circuit.

Compd.	Rs (Ω)	Rct (Ω)
LT-P	31.35	30.08
LT-F	36.19	30.67
LT-S	28.37	27.94
LY-P	33.46	30.41
LY-F	31.21	18.93
LY-S	31.81	11.7

dyes sensitized DSSCs result from the same electrolyte and electrode in both materials and surface area.

The Nyquist spectra exhibit two semicircles which correspond to two peaks observed in Bode spectra. Small semicircles correspond to high-frequency peaks of Bode spectra. Large semicircles at low frequencies correspond to the peak at 1-1k Hz in Bode spectra, which represent the charge-transfer resistance (R_{ct}) at the photoanode/electrolyte interface indicating the charge recombination rate. Larger semicircle and lower-frequency peak relate to higher R_{ct}, suggesting slower electron recombination rate and accordingly the possible higher V_{OC} . The diameters of the large semicircles in Nyquist spectra increase in the order LY-S < LY-F < LT-S < LT-P < LY-P < LT-F, which is consistent with the decreasing frequency order of the peak at 1-1k Hz in Bode spectra and the R_{ct} order in Table 2. These trends roughly agree with the slightly higher V_{OC} of LT-series dyes than LY-series dyes except LT-P and LY-**P** with benzene π -bridge. In fact, LT-series dyes show similar R_{ct} which is very close to that of LY-P while the introduction of BTZ widens the $R_{\rm ct}$ gap among LY-series dyes. $\mbox{LY-F}$ and $\mbox{LY-S}$ have distinctly lower R_{ct} among these carbazole dyes. Therefore, the introduction of benzothiadiazole seems bring forth higher electron recombination rate and accordingly lower V_{OC} in the case of LY-F and **LY-S** with furan and thiophene as π -bridge respectively. However, the presence of benzothiadiazole evokes a decline of electron recombination rate for LY-P, which contributes to higher V_{OC} of **LY-P** than **LT-P** and hence the substantial improvement of the photoelectrical conversion efficiency of LY-P (vide infra).



Fig. 5. Electrochemical impedance spectra for DSSCs based on carbazole dyes. (a)Nyquist plot; (b) Bode plot; (c) equivalent circuit.



Fig. 6. IPCE and J-V curve for DSSCs based on carbazole dyes. (a) IPCE curves for DSSCs based on LT-series dyes; (b) IPCE curves for DSSCs based on LY-series dyes; (c) IPCE curves for DSSCs based on six carbazole dyes; (d) J-V curves for DSSCs based on six carbazole dyes.

3.5. Photovoltaic performance

The action spectra of the incident photo-to-current conversion efficiency (IPCE) for carbazole dyes sensitized DSSCs are shown in Fig. 6(a)–(c). The photovoltaic performances of the carbazole dyes sensitized DSSCs under standard conditions (AM 1.5G, 100 mW cm⁻²) were measured using an iodine electrolyte and the *J*-*V* curves are shown in Fig. 6(d). The detailed photovoltaic parameters of short-circuit photocurrent (*J*_{SC}), open-circuit photovoltage (*V*_{OC}), fill factor (FF) and power conversion efficiency (η) are summarized in Table 3 along with the parameters of N719 sensitized DSSC for comparison.

As mentioned above, the introduction of BTZ contributes to broader absorption spectra and decreased energy gaps, which consequently leads to better light-harvesting capabilities and intramolecular charge transfer abilities of LY-series dyes than LTseries dyes. Therefore, LY-series dyes sensitized DSSCs exhibit broader IPCE spectra than those of LT-series dyes. In addition, benzene π -bridge brings about distinctly narrow IPCE spectra of **LT-P** and **LY-P** relative to their corresponding counterparts with thiophene or furan bridge, which is derived from their narrow absorption spectra both in solution and on TiO₂ film.

Compared with the absorption spectra on $3\,\mu m$ TiO_2 film, carbazole dyes show broader IPCE spectra obtained with $12.0\,\mu m$

Table 3

Parameters for DSSCs based on carbazole dyes: open-circuit photovoltage V _{OC} , short
circuit photocurrent density J _{SC} , fill factor ff, solar energy-to-electricity conversion
efficiency η.

Compd	$Jsc (mA cm^{-2})$	Voc (V)	ff	η %
LT-P	5.41	0.69	0.63	2.35
LT-F	8.43	0.71	0.63	3.74
LT-S	9.26	0.70	0.63	4.14
LY-P	9.14	0.70	0.63	4.05
LY-F	12.22	0.68	0.60	4.96
LY-S	11.27	0.63	0.61	4.35
N719	18.48	0.80	0.45	6.57

nanocrystalline TiO₂ electrodes except **LT-P** and **LY-P** with benzene π -bridge. In LT-series dyes, **LT-F** shows a little better IPCE spectrum than **LT-S** above 380 nm and exhibits the maximum IPCE value 82.3% at 440 nm with over 60% IPCE value among 390–500 nm. However, **LT-S** shows higher IPCE value than **LT-F** among 330–380 nm indicating its high incident photo-to-current conversion efficiency at blue light region, which may contribute to higher *J*_{SC} of **LT-S** than **LT-F**. Distinctly narrower and lower IPCE spectrum is observed for **LT-P**, which leads to its remarkably low *J*_{SC}.

With the incorporation of benzothiadiazole, LY-series dyes exhibit broader IPCE spectra along with relatively lower IPCE value than LT-series dyes (Fig. 6(c)). The onset of IPCE spectra for LTseries dyes is found at 600 nm (LT-S and LT-F) and 550 nm (LT-P); while the responsive region of IPCE spectra for LY-series dyes shift to 675 nm (LY-S and LY-F) and 625 nm (LY-P) respectively. Broader IPCE spectra for LY-series dyes bring about higher I_{SC} (LY-series dyes 9.14-12.22 mA cm⁻²; LT-series dyes 5.41-9.26 mA cm⁻²), suggesting their better light harvesting ability and improved overall electron injection efficiency derived from the presence of benzothiadiazole. LY-F gives over 60% IPCE value from 390 nm to 560 nm and reaches its maximum value of 74.2% at 460 nm, corresponding to its highest *I*_{SC} among these carbazole dyes. Similar to LT-series dyes, LY-F and LY-S exhibit better IPCE spectra than LY-P. Therefore, electron-rich thiophene and furan benefit the light harvesting ability and electron injection efficiency compared with benzene.

On the other hand, the presence of benzothiadiazole prompts the decrease of V_{OC} though it favors the improvement of J_{SC} . V_{OC} is influenced mainly by the electron injection efficiency and the electron recombination rate while JSC depends on the light harvesting ability and the electron injection efficiency. Since LYseries dyes have the increasing J_{SC} and decreasing V_{OC} when compared with LT-series dyes, lower VOC of LY-series dyes may result from their fast electron recombination rate. LY-P is an exception and exhibits superior V_{OC} to LT-P due to its lower electron recombination rate (vide supra). Therefore LY-P gives a significant enhancement of photoelectrical conversion efficiency with the incorporation of benzothiadiazole and the power conversion efficiency of LY-P sensitized DSSC lifts to 4.05% from 2.35% of LT-P sensitized DSSC. Among six carbazole dyes, LY-F with benzothiadiazole auxiliary acceptor and furan π -bridge gives the optimal photovoltaic performance of 4.96% thanks to its highest Isc 12.22 mA cm^{-2} .

4. Conclusion

Three LT-series carbazole dyes were synthesized with Ndimethylfluorenylcarbazole as the electron donor, cyanoacrylic acid as the electron acceptor and benzene, furan and thiophene as π -bridge. Based on LT-series carbazole dyes, three LY-series carbazole dyes were designed and synthesized by incorporating benzothiadiazole into their corresponding counterpart dyes. The incorporation of benzothiadiazole broadens the absorption spectra at long wavelength region and meanwhile favors the blue light harvesting, which contributes to better IPCE spectra and improved J_{SC}. In LT-series carbazole dyes without benzothiadiazole, LT-S with thiophene bridge has apparently superior absorption spectrum to LT-F with furan bridge, ultimately leading to its improved IPCE spectrum and accordingly the optimal photoelectrical conversion efficiency. However, the presence of benzothiadiazole reduces the gap resulting from different π -bridges and **LY-F** with furan bridge exhibits similar absorption spectrum with LY-S with thiophene bridge. Moreover, on TiO2, LY-F exhibits better absorption spectrum than LY-S and hence better IPCE spectrum, which contributes to its superior J_{SC} and accordingly the best photoelectrical conversion efficiency 4.96%. Notably, when with benzene π -bridge, the introduction of BTZ improves both J_{SC} and V_{OC} of **LY-P** which obtain the maximum enhancement of photoelectrical conversion efficiency relative to its counterpart dye LT-P.

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