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Novel D- π -A benzocarbazole dyes with simple structures for efficient dyesensitized solar cells



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Keywords: Benzocarbazole Sensitizers Photovoltaic performance Dye-sensitized solar cells	Three benzocarbazole dyes were synthesized with <i>N</i> -butylbenzocarbazole as the electron donor, benzene, furan and thiophene as π -bridge, and cyanoacrylic acid as the electron acceptor. Their photophysical properties and photovoltaic performance were investigated and compared among three π -bridges. The incorporation of thiophene or furan unit favors intramolecular charge transfer through reducing the energy gap and improving the molecular conjugation due to their electron-rich properties and small volume compared with benzene unit. On the other hand, weakening coplanarity of dye with benzene bridge contributes to the antiaggregation and accordingly increase V_{OC} , though decreases photo-generated current. Among three dyes, dye with furan bridge
	achieves the optimal photovoltaic performance 7.67% due to the highest J_{SC} 15.45 mA cm ⁻² .

1. Introduction

The fast depletion of petroleum reserves along with the growing problem related with their combustion leads to a surge in the demand for clean energy alternatives recently [1]. As the most plentiful and widely distributed renewable energy source, solar energy seems to be a good candidate for the development of the energy production technologies [2]. Therefore, there are many photovoltaic devices developed to convert solar energy into electricity power through solar cells [3]. Nowadays solar cells based on silicon dominate the commercial market, however, their development have been hindered by the demand of highly crystalline silicon and consequent high cost [4]. Therefore, the hybrid solar cells characterized by low material cost and easy manufacturing process have aroused great interest [5].

In various hybrid solar cells, dye-sensitized solar cells (DSSCs) have attracted extensive interests for their good commercial prospects derived from its low fabrication cost, flexibility in the scaling process and good photovoltaic performance [6–8]. In DSSCs, dye molecules absorb the sunlight and inject the electron into the photoanode, which initiates the whole current cycling. Therefore, dyes play an important role in DSSCs. Better light-harvesting ability and electron injection efficiency of dyes are beneficial for the promotion of photoelectric conversion efficiency. A lot of efforts had been made to design various dye sensitizers to optimize the photovoltaic performance of DSSCs.

Earlier studies about dye sensitizers were related to metal organic sensitizers, especially functional ruthenium complexes which were

prepared from the expensive metal through tedious synthetic and purification process [9,10]. Then the researchers have turned the attention to metal-free organic sensitizers which feature high molar extinction coefficient, structure diversity and low cost [11,12]. The typical structure of metal-free organic sensitizers generally consists of the electron donor (D), π -bridge and the electron acceptor (A) to form a D- π -A system. A lot of electron-rich nitrogen-containing heterocycles have been introduced into the sensitizers as the electron donor, such as triarylamine [13-15], carbazole [16-18], indoline [19,20], phenothiazine [21,22] etc. Except the firstly reported vinyl bond, various heterocycles in which thiophene and its derivatives dominate have been selected as π -bridge to help the intramolecular charge transfer from the electron donor to the electron acceptor [23-25]. Cyanoacrylic acid is the most used acceptor, which also play an anchoring role on photoanode. The appropriate combination of the electron donor, π -bridge and electron acceptor offers various kinds of metal-free organic sensitizers.

Carbazole and its derivatives feature electron-rich property and good hole-transporting capability, which are the common candidates for the electron donor of dye sensitizers. Carbazole donors bearing different substitution group combined with a wide array of heterocyclic π -bridges afford a lot of carbazole sensitizers with good photoelectric conversion efficiency [26–28]. Researchers have found that fine adjustment of carbazole sensitizers may tune the optical physical and electrochemical properties, thereby optimizing DSSC performance. For example, when *N*-phenylcarbazole was attached to the C-2 of thiophene

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Scheme 1. Syntheses of benzocarbazole dyes.

bridge instead of C-3, the photoelectric conversion efficiency was increased to 2.40% from 0.34% [29]. In our previous study, varying linking position of 4-phenyl-2-(thiophen-2-yl)thiazole π-bridge to benzene ring of carbazole donor from N atom favors the improvement of the short-circuit current density and open circuit voltage, elevating the photoelectricity conversion efficiency to over 4% from 2% [30]. We also found that the benzene unit in N-phenylcarbazole sensitizers is not coplanar with carbazole unit and helps little to the enlargement of conjugation system [31]. On the other hand, we noticed that benzocarbazole or thieno[3,2-a]carbazole sensitizers achieved improved photoelectric conversion efficiency [26,28]. Therefore, we changed the benzene unit in N-phenylcarbazole to fuse with carbazole ring instead of substitution of N atom and obtained benzocarbazole donor with larger conjugative system and better electron-donating ability. The common used thiophene and furan units were incorporated as π -bridge to further enlarge the conjugative system while benzene π -bridge was also introduced in order to improve the photovoltage. Hence, three benzocarbazole dyes were synthesized with N-butylbenzocarbazole donor, benzene, thiophene, furan π -bridge and cyanoacrylic acid acceptor(Scheme 1). The results show that the photoelectric conversion efficiency has been boosted to 5.10~7.67% from 2.40% through the location variation of benzene ring (Fig. 1).

2. Experimental

2.1. Materials and characterization

Nuclear magnetic resonance spectra were measured on Bruker Avance III 500 MHz with chemical shifts expressed in ppm. Mass spectra were recorded with 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

TiO₂ electrodes and Pt electrodes were purchased from Yingkou Opvtech New Energy Co. Ltd. The TiO₂ electrode was immersed into the dye solution in a cosolvent of MeOH and CHCl₃ (V_{MeOH} : $V_{CHCI3} = 1:10$). After being kept at room temperature for 24 h to assure complete dye uptake, the TiO₂ electrode was rinsed with MeOH to remove excess dye. The dye-loaded TiO₂ electrode and Pt electrode were assembled into a sandwich type cell filled with an electrolyte. The electrolyte used here is composed of the CH₃CN solution of 0.30 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.03 M I₂, 0.07 M LiI, 0.10 M guanidine thiocyanate, and 0.40 M 4-tert-butylpyridine (TBP). The active area of DSSCs was 0.36 cm².

2.3. Photovoltaic characterization

A Keithley digital source meter (Keithley 2420, USA) was used to evaluate the photovoltaic performance of the DSSCs at AM 1.5 G illumination (100 mW/cm²; Sol3A, Newport, USA). The IPCE (monochromatic incident photon-to-current conversion efficiency) spectra were recorded by a Hypermonolight (SM-25, Jasco, Japan). The cyclic voltammetry were recorded at a constant scan rate of 100 mV s⁻¹ with a computer controlled electrochemical analyzer (IviumStat, Holland).



Fig. 1. Structures of N-phenylcarbazole and benzocarbazole sensitizers.

2.4. General procedure for the synthesis of compounds

2.4.1. Synthesis of 6,11-dihydro-5H-benzo[a]carbazole I

3,4-Dihydronaphthalen-1(2 H)-one (0.44 g, 3 mmol) and phenylhydrazine (0.32 g, 3 mmol) were dissolved in EtOH (6 mL) and then concentrated HCl (0.30 mL) was added. The mixture was refluxed for 4 h under N₂. After cooled, the solvent was evaporated to dryness and the residue was recrystallized with cyclohexane-toluene cosolvent (V_{cyclohexane} : V_{toluene} = 1:1) to obtain light yellow solid (0.60 g, 92%). m.p. 130⁻131 °C; ¹H NMR (CDCl₃, 500 M) δ : 8.24 (s, 1 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 7.2 Hz, 1 H), 7.32-7.25 (m, 2 H), 7.20 (td, *J* = 7.2, 0.9 Hz, 2 H), 7.14 (t, *J* = 7.0 Hz, 1 H), 3.13-3.05 (m, 2 H), 3.05-2.96 (m, 2 H).

2.4.2. Synthesis of 11H-benzo[a]carbazole II

Compound I (0.22 g, 1 mmol) and 2,3-Dichloro-5,6-dicyano-1,4benzoquinone (0.30 g, 1.30 mmol) were dissolved in toluene (10 mL). The mixture was stirred for 3 h at room temperature. Then the reactant was washed with NaOH aqueous solution (5%) and saturated NaCl aqueous solution. The solvent was evaporated to dryness and the residue was purified with column chromatography (V_{PE} : $V_{EtOAc} = 10:1$) to give white solid (0.15 g, 70%). m.p. 230⁻²31 °C; ¹H NMR (CDCl₃, 500 M) δ : 8.83 (s, 1 H), 8.16 (dd, J = 8.0, 6.1 Hz, 3 H), 8.04 (d, J = 8.2 Hz, 1 H), 7.69 (d, J = 8.5 Hz, 1 H), 7.65-7.60 (m, 2 H), 7.58-7.54 (m, 1 H), 7.49-7.44 (m, 1 H), 7.33 (t, J = 7.5 Hz, 1 H).

2.4.3. Synthesis of 5-bromo-11H-benzo[a]carbazole III

Compound II (0.43 g, 2 mmol) was dissolved in DMF (8.50 mL) and then the solution of NBS (0.36 g, 2 mmol) in DMF (3 mL) was added slowly under ice bath. After stirred for 4 h, the reactant was diluted with water and extracted with dichloromethane. The organic layers were combined, dried with anhydrous MgSO₄ and filtrated. The solvent was evaporated to dryness and the residue was purified through column chromatography (V_{PE} : V_{EtOAc} = 10:1) to give grey solid (0.53 g, 90%). m.p.146~147 °C; ¹H NMR (CDCl₃, 500 M) δ : 8.87 (s, 1 H), 8.47-8.39 (m, 2 H), 8.14-8.10 (m, 1 H), 8.08 (d, *J* = 7.8 Hz, 1 H), 7.68-7.64 (m, 2 H), 7.59 (d, *J* = 8.1 Hz, 1 H), 7.48 (d, *J* = 7.0 Hz, 1 H), 7.34 (d, *J* = 7.0 Hz, 1 H); HREIMS *m*/*z* 296.0067, 298.0034[M+H]⁺, cacld C₁₆H₁₁BrN for: 296.0075

2.4.4. Synthesis of 5-bromo-11-butyl-11H-benzo[a]carbazole IV

Compound III (0.59 g, 2 mmol) was dissolved in DMSO (2 mL) and mixed with 50% aqueous NaOH solution (1.28 mL). After the slow addition of n-butyl bromide (0.27 mL), the reactant was stirred overnight. The reaction was quenched with water and the precipitate was filtrated. The filtrate cake was purified through column chromatography (V_{PE}: V_{EtOAc} = 10:1) to give white solid (0.39 g, 55%). m.p. 161[~] 162 °C; ¹H NMR (500 MHz, CDCl₃) δ : 8.55-8.46 (m, 3 H), 8.11 (d, *J* = 7.8 Hz, 1 H), 7.71-7.63 (m, 2 H), 7.59-7.50 (m, 2 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 4.73 (t, *J* = 7.5 Hz, 2 H), 2.07-2.01 (m, 2 H), 1.59-1.51 (m, 2 H), 1.04 (t, *J* = 7.4 Hz, 3 H); HREIMS *m*/*z* 352.0700, 354.0674 [M + H]⁺, cacld C₂₀H₁₉BrN for: 352.0701

2.4.5. Synthesis of 4-(11-butyl-11H-benzo[a]carbazol-5-yl)benzaldehyde Va

Compound IV (0.71 g, 2 mmol), 4-formyphenylboronic acid (0.36 g, 2.40 mmol) and Pd(PPh₃)₄ (0.23 g, 0.20 mmol) were dissolved in THF (10 mL) and aqueous K₂CO₃ solution (4 mL, 2 M) was added dropwisely. The reactant was refluxed for 10 h under N₂ and then quenched with water. The mixture was extracted with CH₂Cl₂ and the organic layers were combined. After the solvent was evaporated to dryness, the residue was purified through column chromatography (V_{PE}: V_{EtOAc} = 10:1) to give yellow oil (0.53 g, 70%). ¹H NMR (500 MHz, CDCl₃) δ : 10.16 (s, 1 H), 8.63 (d, *J* = 8.5 Hz, 1 H), 8.17-8.16 (m, 2 H), 8.07-8.05 (m, 3 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 7.62 (d, *J* = 8.3 Hz, 1 H), 7.56-7.49 (m, 2 H), 7.35 (t, *J*

= 7.4 Hz, 1 H), 4.86 (t, J = 7.5 Hz, 2 H), 2.16-2.09 (m, 2 H), 1.65-1.57 (m, 2 H), 1.08 (t, J = 7.4 Hz, 3 H); HREIMS m/z 378.1852 [M+H]⁺, cacld C₂₇H₂₄NO for: 378.1858.

2.4.6. Synthesis of 5-(11-butyl-11H-benzo[a]carbazol-5-yl)furan-2carbaldehyde **Vb**

Compound IV (0.71 g, 2 mmol), (5-formylfuran-2-yl)boronic acid (0.34 g, 2.40 mmol) and Pd(PPh₃)₄ (0.23 g, 0.20 mmol) were dissolved in THF (10 mL) and aqueous K₂CO₃ solution (4 mL, 2 M) was added dropwisely. The reactant was refluxed for 10 h under N₂ and then quenched with water. The mixture was extracted with CH₂Cl₂ and the organic layers were combined. After the solvent was evaporated to dryness, the residue was purified through column chromatography (V_{PE}: V_{EtOAc} = 10:1) to give orange oil (0.50 g, 68%). ¹H NMR (500 MHz, CDCl₃) & 9.76 (s, 1 H), 8.58-8.55 (m, 3 H), 8.20 (d, *J* = 7.8 Hz, 1 H), 7.70-7.67 (m, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.49 (d, *J* = 3.7 Hz, 1 H), 7.37 (t, *J* = 7.0 Hz, 1 H), 6.94 (d, *J* = 3.6 Hz, 1 H), 4.78 (t, *J* = 8.0 Hz, 2 H), 2.11-2.05 (m, 2 H), 1.62-1.55 (m, 2 H), 1.06 (t, *J* = 7.4 Hz, 3 H); HREIMS *m*/z 368.1643 [M+H]⁺, cacld C₂₅H₂₂NO₂ for: 368.1651.

2.4.7. Synthesis of 5-(11-butyl-11H-benzo[a]carbazol-5-yl)thiophene-2-carbaldehyde Vc

Compound IV (1.06 g, 3 mmol), (5-formylthiophen-2-yl)boronic acid (0.56 g, 3.60 mmol) and Pd(PPh₃)₄ (0.35 g, 0.30 mmol) were dissolved in THF (15 mL) and aqueous K₂CO₃ solution (6 mL, 2 M) was added dropwisely. The reactant was refluxed for 10 h under N₂ and then quenched with water. The mixture was extracted with CH₂Cl₂ and the organic layers were combined. After the solvent was evaporated to dryness, the residue was purified through column chromatography (V_{PE}: V_{EtOAc} = 10:1) to give yellowgreen liquid (0.76 g, 66%); ¹H NMR (500 MHz, CDCl₃) δ :10.00 (s, 1 H), 8.59 (d, *J* = 8.5 Hz, 1 H), 8.54-8.48 (m, 1 H), 8.38 (d, *J* = 8.1 Hz, 1 H), 8.32 (s, 1 H), 8.16 (d, *J* = 7.8 Hz, 1 H), 7.89 (d, *J* = 3.7 Hz, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 4.0 Hz, 1 H), 7.37 (d, *J* = 7.1 Hz, 1 H), 4.80 (t, *J* = 7.5 Hz, 2 H), 2.12-2.06 (m, 2 H), 1.63-1.55 (m, 2 H), 1.07 (t, *J* = 7.5 Hz, 3 H); HREIMS *m*/*z* 384.1418 [M+H]⁺, cacld C₂₅H₂₂NOS for: 384.1422

2.4.8. Synthesis of 3-(4-(11-butyl-11H-benzo[a]carbazol-5-yl)phenyl)-2cyanoacrylic acid YHQ-B

Va (0.19 g, 0.50 mmol) and cyanoacetic acid (0.09 g, 1.05 mmol) were dissolved in CHCl₃ (6 mL) and piperidine (0.50 mL) was added. The reactant was refluxed for 10 h under N2. Then the mixture was washed with diluted HCl and then evaporated to dryness. The residue was purified through column chromatography (V_{HAc}: V_{MeOH}: V_{CH2Cl2} = 1:4:400) to give brown solid (0.12 g, 54%). m.p. 224~226 °C; ¹H NMR (500 MHz, DMSO) δ : 8.71 (d, J = 8.7 Hz, 1 H), 8.30-8.27 (m, 2 H), 8.10-8.07 (m, 3 H), 8.01 (d, J = 8.5 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.75-7.70 (m, 3 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.29 (t, J = 7.4 Hz, 1 H), 4.93 (t, J = 7.2 Hz, 2 H), 1.97-1.91 (m, 2 H), 1.49-1.42 (m, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); ¹³C NMR (125 MHz, DMSO) & 163.82, 163.78, 147.81, 143.94, 140.49, 133.51, 131.57, 130.87(2C), 130.69, 129.57(2C), 126.72, 125.82, 125.11(2C), 122.46, 122.26, 121.96, 120.56, 119.77, 119.67, 119.03, 118.20, 112.46, 109.98, 45.00, 31.74, 19.54, 13.79; HREIMS m/z 445.1916 [M+H]⁺, cacld C₃₀H₂₅N₂O₂ for: 445.1916

2.4.9. Synthesis of 3-(5-(11-butyl-11H-benzo[a]carbazol-5-yl)furan-2-yl)-2-cyano- acrylic acid YHQ-F

Vb (0.73 g, 2 mmol) and cyanoacetic acid (0.36 g, 4.20 mmol) were dissolved in CHCl₃ (10 mL) and piperidine (0.70 mL) was added. The reactant was refluxed for 10 h under N₂. Then the mixture was washed with diluted HCl and then evaporated to dryness. The residue was purified through column chromatography (V_{HAc}: V_{MeOH}: V_{CH2Cl2} = 1:4:400) to give orange solid (0.34 g, 39%); m.p. 215~217 °C;

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¹H NMR (500 MHz, DMSO) δ : 8.82 (s, 1 H), 8.73-8.69 (m, 2 H), 8.27 (d, J = 7.8 Hz, 1 H), 7.88-7.86 (m, 2 H), 7.79 (t, J = 7.5 Hz, 1 H), 7.70 (t, J = 7.5 Hz, 1 H), 7.54 (t, J = 7.3 Hz, 1 H), 7.40 (d, J = 3.5 Hz, 1 H), 7.34 (t, J = 7.4 Hz, 1 H), 7.28-7.24 (m, 1 H), 4.93 (t, J = 7.5 Hz, 2 H), 1.97-1.88 (m, 2 H), 1.48-1.39 (m, 2 H), 0.94 (t, J = 7.5 Hz, 3 H); ¹³C NMR (125 MHz, DMSO) δ : 164.16, 158.77, 147.75, 140.74, 136.17, 134.72, 129.26, 126.39, 126.10(2C), 125.52, 122.71, 122.26, 121.90(2C), 121.46, 120.25(2C), 119.56, 118.29, 118.25, 117.66, 112.40, 110.28, 45.10, 31.57, 19.47, 13.74; HREIMS m/z 435.1702 [M+H]⁺, cacld C_{28H23N2O3} for: 435.1709

2.4.10. Synthesis of 3-(5-(11-butyl-11H-benzo[a]carbazol-5-yl)thiophen-2-yl)-2- cyanoacrylic acid YHQ-S

Vc (1.15 g, 3 mmol) and cyanoacetic acid (0.54 g, 6.30 mmol) were dissolved in CHCl₃ (15 mL) and piperidine (1 mL) was added. The reactant was refluxed for 10 h under N2. Then the mixture was washed with diluted HCl and then evaporated to dryness. The residue was purified through column chromatography (V_{HAc}: V_{MeOH}: $V_{CH2Cl2} = 1:4:400$) to give orange solid (0.40 g, 29%); m.p. 220²221 °C; ¹H NMR (500 MHz, DMSO) δ : 13.79 (bs, 1 H), 8.74 (d, J = 8.6 Hz, 1 H), 8.62 (s, 1 H), 8.54 (s, 1 H), 8.36 (d, J = 7.8 Hz, 1 H), 8.31 (d, J = 8.4 Hz, 1 H), 8.17 (d, J = 4.0 Hz, 1 H), 7.87 (d, J = 8.5 Hz, 1 H), 7.80 (t, J=7.3 Hz, 1 H), 7.68 (t, J = 8.0 Hz, 1 H), 7.60 (d, J = 3.6 Hz, 1 H), 7.54 (t, J = 7.4 Hz, 1 H), 7.36-7.30 (m, 1 H), 4.95 (t, J = 7.3 Hz, 2 H), 1.98-1.88 (m, 2 H), 1.49-1.41 (m, 2 H), 0.94 (t, J = 7.4 Hz, 3 H); ¹³C NMR (125 MHz, DMSO) & 163.77, 163.46, 146.84, 146.77, 140.59, 140.42, 139.40, 136.34, 135.16, 134.39, 130.50, 129.33, 128.68, 126.30, 125.83, 125.44, 122.68, 122.12, 121.95, 120.08, 119.97, 118.03, 116.58, 110.16, 45.06, 31.63, 19.50, 13.76; HREIMS m/z 451.1476 [M +H]⁺, cacld C₂₈H₂₃N₂O₂S for: 451.1480

3. Results and discussion

3.1. Syntheses

Benzocarbazole **II** was prepared from 3,4-dihydronaphthalen-1(*2H*)-one and phenylhydrazine through Fischer indole synthesis and the following oxidation reaction. Benzocarbazole was brominated with NBS to obtain intermediate **III** which was substituted by 1-bromobutane on N atom to give *N*-butylbenzocarbazole bromide **IV**. **IV** was coupled with formylarylboronic acid through Suzuki coupling to synthesize aldehyde intermediates **V**. Knoevenagel condensation between aldehyde intermediates and cyanoacetic acid affords three benzocarbazole dyes **YHQ-B**, **YHQ-F** and **YHQ-S**, respectively.

3.2. Optical properties

In CHCl₃-CH₃OH solution the light-harvesting abilities of three benzocarbazole dyes were measured. The corresponding absorption spectra and photophysical data were listed in Fig. 2 and Table 1, respectively. Above 400 nm, YHQ-F shows the broadest absorption range and exhibits a peak at 450 nm with a molar extinction coefficient 21366 M^{-1} cm⁻¹. This peak is ascribed to the transition absorption of intramolecular charge transfer (ICT) from the benzocarbazole donor to cvanoacrylic acid acceptor. A hypsochromic shift of 17 nm was observed in the case of YHQ-S along with an evident attenuation of molar extinction coefficient. This may be attributed to the smaller resonance energy of the furan than thiophene, which ensures a more effective conjugation in the π -bridge of **YHQ-F**. When π -bridge was changed into benzene unit, YHQ-B exhibits an ICT absorption at 367 nm with a lower molar extinction coefficient 10960 $M^{-1} cm^{-1}$ than **YHQ-S**. As can be seen, π -bridge has a considerable influence on the light-harvesting ability of these benzocarbazole dyes. The electron-rich furan and thiophene units have lower electron delocalization energy and at the same time their five-atom structures have smaller size related to six-member benzene unit. This contributes to the better conjugation and molecular

coplanarity leading to more efficient intramolecular charge transfer. Therefore, **YHQ-F** and **YHQ-S** show the red-shifted ICT absorption and absorb more photons from the visible region, indicating their superior light-harvesting ability to **YHQ-B**. The optical parameters of **OM1** were also listed in Table 1 for comparison. **YHQ-S** exhibits a red shift of 42 nm when compared with **OM1**, indicating it's more efficient intramolecular charge transfer. This improved ICT may be owing to the better electron-donating ability of benzocarbazole than *N*-phenylcarbazole, since **YHQ-S** has the same thiophene bridge and cyanoacrylic acid acceptor with **OM1**.

On TiO₂, the carboxylic acid group in dye molecule deprotonates to form carboxylate-TiO₂ unit. Dye molecules form *H*-aggregates with parallel arrangement or *J*-aggregates with head to tail arrangement on TiO₂. The formation of aggregates often broadens the absorption spectra on TiO₂ related to in solution. The absorption spectra of three benzocarbazole dyes on TiO₂ were measured and listed in Fig. 2(b). As can be seen in Fig. 2(b), the absorption spectrum onsets of three benzocarbazole dyes on TiO₂ shift bathochromically. In particular, **YHQ-F** exhibits a 50 nm broadening of the absorption spectrum on TiO₂ and its absorption spectrum onset shifts to 600 nm on TiO₂ from 550 nm in solution, which should be ascribed to its highest loading amount on TiO₂ (Table 1).

In addition, the ICT absorption shift is observed on TiO_2 for three benzocarbazole dyes. **YHQ-B** exhibits a red shift of 4 nm while **YHQ-F** and **YHQ-S** show the blue shift of 16 nm and 46 nm, respectively. Due to a large dihedral angle between benzocarbazole unit and benzene bridge (*vide infra*), **YHQ-B** shows inferior coplanarity and tends to form *J*-aggregates through head to tail connection, which leads to the bathochromic shift of the ICT absorption. On the other hand, when sixmember benzene bridge was replaced by five-member furan or thiophene bridge, the dihedral angle between benzocarbazole and π -bridge decreased and better coplanarity was achieved in **YHQ-F** and **YHQ-S**. Thus, they are easy to arrange in *H*-aggregates inducing the hypsochromic shift of the ICT absorption.

Though the blueshift of ICT peak was observed, YHQ-F and YHQ-S still exhibit larger maximum absorption wavelength than YHQ-B on TiO₂. Broader absorption spectra in the visible region were observed for YHQ-F and YHQ-S when compared with YHQ-B, indicating superior light-harvesting ability of the former. Thanks for the best light-harvesting ability and the largest loading amount, YHQ-F shows the broadest absorption spectrum on TiO₂ among three benzocarbazole dyes, suggesting its most efficient photon absorption and conversion.

3.3. Theoretical calculation

To better understand the relationship between the molecular structure and the photophysical properties, quantum chemical calculations of three benzocarbazole dyes were performed by using spin-restricted DFT method with B3LYP, in conjunction with 6-311+G(d,p)basis set. The singlet ground-state geometrical optimizations of three dyes were performed in CHCl₃ solvent, which has been modeled using conductor-like polarizable continuum model. Based on the optimized geometries, the molecular orbitals (MOs) of three compounds were calculated at the same level. The HOMO energy level (E_{HOMO}) of each compounds are taken from the Kohn-Sham eigenvalues calculated from the DFT. TDDFT calculation of the single excitation energies was also performed at the ground states. In the calculation coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP) was used which is a long range corrected version of B3LYP, and the basis set is 6-31 + G(d). Then the energy gaps (E_g) were estimated based on the singlet-singlet electronic transition energies. The LUMO energy level (E_{LUMO}) can be obtained according to the equation $E_{LUMO} = E_{HOMO}(DFT) + E_g(TDDFT)$. The calculated E_{LUMO} of three compounds are in good agreement with the experimental data. All the calculations of both ground and excited states were performed within the Gaussian 09 quantum chemical package.



Fig. 2. UV-vis absorption spectra of benzocarbazole dyes. (a) in CHCl₃-CH₃OH solution (v:v = 10:1); (b) on TiO₂.

Table 1	
Optical properties of benzocarbazole	e dyes.

Compd	$\lambda_{max} a / (nm)$	ϵ^{a} /(10 ⁴ M ⁻¹ ·cm ⁻¹)	λ _{max} ^b / (nm)	λ _{em} ^c / (nm)	Dye loading amount/ $(mol \cdot cm^{-2})$
YHQ-B YHQ-F YHQ-S OM1	367 450 433 391	1.10 2.14 1.29 3.83	371 434 387 -	550 576 578 -	1.73*10 ⁻⁷ 2.17*10 ⁻⁷ 2.00*10 ⁻⁷

maximum absorption wavelength λ_{max} and molar extinction coefficient at λ_{max} of dyes measured in CH₃Cl-CH₃OH cosolvent (V _{CH3Cl}: V _{CH3OH} = 10:1).

maximum absorption wavelength λ_{max} of dyes on sensitized TiO₂ electrodes.

^c maximum emission wavelength measured in CH₃Cl-CH₃OH cosolvent (V _{CH3CI}: V _{CH3OH} = 10:1).

The optimized geometrical structures of three dyes were listed in Fig. 3. As can be seen from three geometrical structures, π -bridges are coplanar with cyanoacrylic aicd acceptor while there are large dihedral angles between the benzocarbazole donor and π -bridges. These dihedral angles are 50.8°, 32.3°, and 45.6° for YHQ-B, YHQ-F and YHQ-S, respectively, and rank in the order of YHQ-B > YHQ-S > YHQ-F. The large dihedral angle between the donor and π -bridge may hamper the conjugation action of the whole molecule and lead to inferior ICT. Therefore, YHQ-F with the smallest dihedral angle is the easiest to transfer the electron from the electron donor to the electron acceptor leading to the largest ICT absorption wavelength.



Fig. 4. Energy level of the HOMO and LUMO of benzocarbazole dyes at B3LYP/ 6-31 G(d) in CHCl₃ solvent.

YHQ-S

YHQ-F

YHQ-B

Fig. 4 shows the energy level of the frontier molecular orbitals for three benzocarbazole dyes. LUMO energy levels of three dyes are located at $-3.66^{-3.36}$ eV, which is higher than the TiO₂ CB energy level (-4.0 eV); while HOMO energy levels are observed at -6.85~-6.75 eV and lower than the potential of the redox couple I_3^{-}/I^{-} (-4.9 eV). Thus, the excited dyes can inject the electrons efficiently into the TiO₂ CB and meanwhile the oxidized dyes may accept the electrons from the electrolyte to be reduced successfully. The introduction of electron-rich thiophene or furan unit to replace benzene unit shifts both HOMO and



YHO-S

Fig. 3. Optimized geometries of benzocarbazole dyes at the B3LYP/6-311+G(d,p) level.

 Table 2

 Energy levels of benzocarbazole dves.

lifergy revers of benzoeurbazore dyes.						
Compd.	Experimental ^a (eV)			Calculated ^d (eV)		
	HOMO ^a	E_{0-0}^{b}	LUMO ^c	НОМО	E ₀₋₀	LUMO
YHQ-B YHQ-F	-5.58 -5.62	2.76 2.43	-2.82 - 3.19	- 6.75 - 6.77	3.39 3.11	-3.36 -3.66
YHQ-S	-5.44	2.48	-2.96	-6.85	3.32	-3.53

 $^{\rm a}$ The oxidation potential $E_{\rm ox}$ in DMF was determined from cyclic voltammograms and used to describe the ground-state energy HOMO.

 $^b~E_{0\text{-}0}$ was calculated from $E_{0\text{-}0}=1240/\,\lambda_{int}$ and λ_{int} was the intersection of the normalized absorption and emission spectra.

^c E_{LUMO} was calculated from E_{ox}-E₀₋₀.

^d Calculated in CHCl₃ solvent.

LUMO down, especially the LUMO. The greatly downshifted LUMO decreased the energy gap of **YHQ-F** and **YHQ-S** leading to the easy ICT transition which was proved by their longer ICT absorption wavelength in Table 1. Cyclic voltammograms were performed to obtain the experimental value of energy levels, which basically agree with the calculated values (Table 2). Compared with that of **OM1** (-5.65 eV) [29], HOMO levels of YHQ-series dyes (-5.62~-5.44 eV) have been upshifted, which further prove the better electron-donating ability of benzo-carbazole than *N*-phenylcarbazole.

Frontier molecular orbitals of benzocarbazole dyes were listed in Fig. 5. The HOMO of three dyes mainly delocalize over the benzocarbazole donor and partially stretch out on the π -bridge. The LUMO are mainly confined to the cyanoacrylic acid acceptor and π -bridge, which exhibit a good overlap over π -bridge with the HOMO, favoring the efficient electron excitation. Comparison of the HOMO population shows that dye with furan bridge has more electron distribution on π -bridges than dyes with thiophene or benzene bridge, which may result in better overlap between HOMO and LUMO of **YHQ-F**. Better overlap of frontier molecular orbitals improves intramolecular charge transfer, which also favor the redshift of ICT absorption peak.

3.4. Photovoltaic performance

Three benzocarbazole dye sensitized DSSCs were fabricated with

 I_3^-/I^- electrolyte. Their related action spectra of the incident photo-tocurrent conversion efficiency (IPCE) were measured and shown in Fig. 6(a). The trend of IPCE spectra of three benzocarbazole dye sensitized DSSCs are similar to that of absorption spectra on TiO₂. In IPCE measurement, as the TiO₂ film thickness increases to 18 um from 1 um when absorption spectra measured, the loading amount of dye continually increase, which extends the IPCE responsive range. **YHQ-B** sensitized DSSC exhibits an IPCE onset at about 600 nm with an extension by 50 nm compared with the absorption spectrum on TiO₂. Larger extension of the onsets was observed in the case of the other two benzocarbazole dyes: **YHQ-F** and **YHQ-S** sensitized DSSCs show the IPCE response till 700 nm and 675 nm respectively due to their higher loading amount.

All benzocarbazole dye sensitized DSSCs gave the maximum IPCE value over 70%. Among three DSSCs, **YHQ-F** sensitized DSSC displays a high plateau over 60% from 380 to 580 nm with a maximum IPCE value of 76% at 466 nm, indicating its superior incident photo-to-current conversion efficiency and accordingly better J_{SC} . For the DSSC based on **YHQ-S**, IPCE values higher than 60% were observed in the range of 385–556 nm with a similar maximum IPCE value 74% at 464 nm to that of **YHQ-F**. However, DSSC based on **YHQ-S** exhibits a little narrower IPCE responsive range than that of **YHQ-F**. Though it exhibits a comparable maximum IPCE value with DSSC based on **YHQ-S**, **YHQ-B** sensitized DSSC shows the narrowest IPCE spectrum among three DSSCs suggesting its least photon harvest.

J-V curves of DSSCs based on three benzocarbazole dyes were evaluated under standard conditions (AM 1.5 G, 100 mW·cm⁻²) and shown in Fig. 6(b). The corresponding parameters V_{OC} (open-circuit photovoltage), J_{SC} (short circuit photocurrent density), *ff* (fill factor) and η (solar energy-to-electricity conversion) were listed in Table 3. The corresponding parameters of **OM1** were also listed in Table 3 for comparison. As can be seen in Table 3, YHQ-series dyes achieved higher J_{SC} (8⁻¹⁶ mA·cm⁻²) than **OM1** (5.85 mA·cm⁻²). Especially, J_{SC} of **YHQ-S** is more than double that of its *N*-phenylcarbazole counterpart **OM1**. Moreover, higher V_{OC} (above 0.7 V) was observed in YHQ-series dyes when compared with **OM1** (0.66 V). We presumed that better electrondonating ability of benzocarbazole benefits the intramolecular charge transfer and accordingly the electron injection into TiO₂ CB, which contribute to the increase of J_{SC} and V_{OC} of YHQ-series dyes.



Fig. 5. Frontier molecular orbitals (HOMO and LUMO) of benzocarbazole dyes.



Fig. 6. IPCE curves (a) and current-potential (J-V) curves (b) for DSSCs based on benzocarbazole dyes.

Table 3Parameters for DSSC based on benzocarbazole dyes.

Comd.	Voc (V)	Jsc (mA·cm ^{−2})	ff	η%
YHQ-B	0.78	8.42	0.78	5.10
YHQ-F	0.76	15.45	0.65	7.67
YHQ-S	0.73	13.30	0.68	6.58
OM1	0.66	5.85	0.62	2.40

 J_{SC} ranks by the order of **YHQ-F** > **YHQ-S** > **YHQ-B**, which agrees well with their IPCE responsive range. Thanks to its highest IPCE maximum value and broadest IPCE responsive range, **YHQ-F** sensitized DSSC achieves the highest J_{SC} of 15.45 mA·cm⁻². Lower IPCE response of DSSC based on **YHQ-S** from 380 to 700 nm than that of **YHQ-F** lowers its J_{SC} to 13.30 mA·cm⁻². **YHQ-B** sensitized DSSC exhibits the lowest J_{SC} of 8.45 mA·cm⁻², which may impair its photoelectric conversion efficiency. Similar with our previous report [31,32], with benzene π -bridge, **YHQ-B** achieves the highest V_{OC} of 0.78 V due to its improved antiaggregation effect derived from its inferior coplanarity. V_{OC} follows the order of **YHQ-B** > **YHQ-F** > **YHQ-S** and **YHQ-S** sensitized DSSC shows the smallest V_{OC} among three DSSCs. Therefore, due to its highest J_{SC} and better V_{OC} , **YHQ-F** achieves the best photoelectric conversion efficiency 7.67%.

Electrochemical impedance spectroscopy (ESI) was usually used to investigate the interfacial charge transfer process, which can help to understand the recombination rate and the lifetime of injected electrons on TiO₂ in the DSSC. Fig. 7 listed the Nyquist diagram of three DSSCs based on YHQ-series dyes measured at standard illumination (100 mW



Fig. 7. Nyquist phase plots for the DSSCs measured under illumination.

cm⁻², AM 1.5 G) conditions. In Fig. 7, YHQ-S sensitized DSSC shows two semicircles: the right semicircle represents the electron transfer at the TiO₂/dye/electrolyte interfaces while the left semicircle corresponds to the redox reaction at the platinum counter electrode. However, only one semicircle is observed in the case of YHQ-B and YHQ-F sensitized DSSCs. The redox reaction at the platinum counter electrode in DSSCs based on YHQ-B and YHQ-F may be too quick when compared with the electron transfer at the TiO2/dye/electrolyte interfaces, which leads to only the presence of one semicircle relates to the electron transfer at the TiO₂/dye/electrolyte interfaces [33]. Using an equivalent circuit (shown in the inset of Fig. 7), the corresponding R_{ct} which represents electron transport resistances at the TiO₂/dye/electrolvte interface was analyzed by software (ZSimpWin). R_{ct} of three DSSCs follows the order: YHQ-S (15.0 Ω) > YHQ-F (14.3 Ω) > YHQ-B (12.6 Ω). Low electron transport resistance of YHQ-B sensitized DSSC indicates better electron collection efficiency. This may be attributed to its antiaggregation effect derived from its inferior coplanar structure, which reduces the charge recombination rate and contributes to the promotion of V_{OC} . The results agreed with the variation trend of V_{OC} in Table 3.

4. Conclusion

Benzocarbazole core was constructed from 3,4-dihydronaphthalen-1(2 H)-one and phenylhydrazine through Fischer Indole synthesis and selected as the electron donor after the nucleophilic substitution with 1bromobutane. Then benzene, furan and thiophene π -bridges were incorporated through Suzuki coupling respectively. After the condensation with cyanoacetic acid, three D-π-A benzocarbazole sensitizers were prepared. The absorption spectra in solution and on ${\rm TiO}_2$ were measured and thiophene or furan π -bridge endows the sensitizer with broader absorption spectra and bathochromic ICT absorption peak. Theoretical calculation based on DFT and TD-DFT shows that dyes with thiophene or furan π -bridge exhibit better coplanarity, increased overlap between HOMO and LUMO, and decreased energy gap, which account for their better light harvesting ability than dye with benzene bridge. Superior light harvesting ability brings about improved J_{SC} and cell fabricated with dye bearing furan bridge shows the highest J_{SC} . On the other hand, the presence of benzene bridge brings about weakening coplanarity, which favors the antiaggregation and accordingly improve V_{OC} . Among DSSCs based on three benzocarbazole dyes, J_{SC} preponderates over V_{OC} in determining the photovoltaic performance, consequently dye with thiophene or furan bridge exhibits higher photoelectric conversion efficiency than dye with benzene bridge. Compared with the similar N-phenylcarbazole sensitizer, three benzocarbazole sensitizers achieve distinctly higher J_{SC} and better V_{OC} , which contributes to the significant promotion of photoelectric conversion efficiency.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019.03. 015.

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