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Synthesis, photophysical and electrochemical properties of two novel carbazole-based dye molecules





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HIGHLIGHTS

- We designed and synthesized two novel carbazole-based dye molecules.
- The dye D4 containing thiophene group showed better photoelectronic and photovoltaic properties than D3.
- The two dyes could be applied as sensitizers in nano-TiO₂ DSSCs.

G R A P H I C A L A B S T R A C T



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ABSTRACT

Two carbazole-based dye molecules: 3-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-2-cyano-acylic acid (D3) and 3-[5-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-thiophen-2-yl]-2-cyan-acylic acid (D4) were synthesized by an approach from carbazole derivate using Vilsmeier-Haack, Suzuki cross-coupling and Knoevenagel reactions. Their physical and electrochemical properties were investigated. D3 and D4 exhibit different optical properties, such as UV absorption, photoluminescence, fluorescence quantum yield and fluorescence lifetime in different solvents. Compared with D3 without a thiophene unit, the maximum absorption wavelength of D4 red-shift obviously and its fluorescence intensity is also enhanced. A shift of the E_{HOMO} and E_{LUMO} is observed for D3 (E_{HOMO} = 2.06 V, E_{LUMO} = -1.39 V vs. NHE) and D4 (E_{HOMO} = 1.73 V, E_{LUMO} = -1.33 V vs. NHE). D3 and D4 can be used as dyes for dye-sensitized solar cells (DSSCs) with TiO₂ nanomaterial because their E_{HOMO} are lower than the conduction band edge of TiO₂ [-0.5 V (vs. NHE)] and their E_{LUMO} are higher than the I^{3-}/I^{-} redox potential [0.42 V (vs. NHE)].

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Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the last 15 years owing to their prospect of high energy conversion efficiency and low production cost [1–4]. Recently, several groups have developed metal free organic sensitizers to overcome the prohibitive cost of ruthenium metal complexes, and the impressive photovoltaic performance has been obtained with some organic coumarin [5–6], indoline [7–8], oligoene [9–11], merocyanine [12], and hemicyanine [13] dyes. Carbazole is relatively easy to functionalize the carbazolyl moiety at the 3-, 6-, or 9-positions for tuning its properties. Carbazole derivative is a kind of promising candidates for photoluminescence and electroluminescence materials as the hole-transporting materials (HTMs) for organic light-emitting diodes (OLEDs) due to the high charge mobility [14–15]. The design and synthesis of functional dyes have become a focus of current research in view of their potential applications as sensitizers in DSSCs technologies [16–17]. Organic molecules with a wide range of absorption in the visible region and containing an

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anchoring group such as cyanoacylic acids are ideal candidates as sensitizers [18]. The DSSCs process requires that these dyes absorb sunlight and excite electron from HOMO to LUMO state. This excited electron is then injected into the conduction band of TiO_2 in a femtosecond life time by the anchoring group and in this process the dye gets oxidized. Then the oxidized dye is neutralized to ground state by I_3^-/I^- redox system [19].

In this paper, we report the synthesis of two novel carbazole-based molecules, 3-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-2-cyano-acylic acid (D3) and 3-[5-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-thiophen-2-yl]-2-cyano-acylic acid (D4), which were both substituted with benzoth-iazole at 3-position of carbazole, and decorated by cyanoacetic acid at 6-position. The benzothiazole moiety is well-known as an excellent acceptor [20-23]. It gives rise to a donor- π -acceptor type compound [21-23] due to its potential role in the modulation of the HOMO-LUMO gap. We introduced a thiophene unit between the carbazole and cyanoacetic acid on the principle of extension of the π -bridge which can make electron delocalize to a plurality of atoms, reduce the π - π * energy, increase the molar extinction coefficient value and promote the maximum absorption wavelength red shift.

Experimental

Materials and instruments

Reagents were purchased as analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification unless otherwise state. Dimethylformamide (DMF) was freshly distilled from molecular sieve.

¹H NMR spectra were obtained on an AV-400 spectrometer (Bruker, Switzerland). Chemical shifts (δ) were given in ppm relative to CDCl₃ 7.26 (1H) or DMSO-d₆ 2.54 (1H). Elemental analysis were determined on a Vario ELIII spectrometer (Elementar, Germany). UV-Vis absorption spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). Fluorescence emission spectra were recorded on a LS-55 FL spectrophotometer (PerkinElmer, USA). The fluorescence quantum yields were calculated using quinine sulfate in 0.01 M H₂SO₄ solution as a standard at room temperature based on the literature [24]. The fluorescence decay behaviors were recorded on a FluoroMax-4P full functional transient and steady-state fluorescence spectrometer (HORIBA Jobin Yvon, France). Cyclic voltammetry (CV) analysis was recorded on a CHI660d electrochemical workstation (Chenhua, China), the measurements were carried out with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and a saturated calomel reference electrode.

Synthesis

9H-hexylcarbazole (2)

1.0 g NaH was added in batches to the stirring solution of carbazole (4.0 g, 24 mmol) in anhydrous DMF. Then 4 mL (28 mmol) 1bromohexane in 15 mL DMF was added dropwise under stirring at 80 °C for 3 h. When the mixture was cooled down to room temperature, it was poured into water and adjusted the pH = 7 with 1:1(HCl/H₂O, v/v) concentrated hydrochloric acid. The product was obtained by filtering and recrystallization from ethanol as an acicular crystal 6.35 g. The yield was 76.5%. ¹H NMR (Fig. S1, 400 Hz, CDCl₃) δ (pm): 8.09 (d, *J* = 7.60 Hz, 2H), 7.38–7.48(m, 4H), 7.21(d, *J* = 8.00 Hz, 2H), 4.28(t, 2H), 1.86(m, 2H), 1.33(m, 6H), 0.86(t, 3H). FT-IR (Fig. S2, KBr, cm⁻¹): 3049(=C-H), 2856– 2953(-CH₂-, -CH₃), 1459(-CH₃), 1323(-CH₂-), 1621–1594 (structure of carbazole).

3-formyl-9H-hexylcarbazole (3)

To a stirring solution of compound 2 (2.51 g, 10 mmol) in anhydrous DMF at ice-water bath, phosphorus oxychloride (POCl₃, 0.2 mol) was added, and the mixture stirred for another 30 min. The mixture was warmed to 70 °C for 2 h and then stirred for overnight at room temperature. It was poured rapidly into ice water and neutralized with potassium bicarbonate. The solution was extracted with ethyl acetate $(3 \times 50 \text{ mL})$ and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (neutral alumina; ethyl acetate/petroleum ether, 1/10, v/v) to give a light yellow solid **2** 1.60 g. Yield: 57.3%. ¹H NMR (Fig. S3, 400 Hz, CDCl₃) δ (pm): 10.10(s, 1H), 8.61(s, 1H), 8.16(d, J = 7.60 Hz, 1H), 8.01(d, J = 8.40 Hz, 1H), 7.45-7.55(m, 3H), 7.32(t, 1H), 4.33(t, 2H), 1.85-1.93(m, 2H), 1.26-1.42(m, 6H), 0.86(t, 3H). FT-IR (Fig. S4, KBr, cm⁻¹): 1692(-C=O), 2953-2862(-CH₃, -CH₂-), 1375(-CH₃), 1472(-CH₂-), 1621-1594(structure of carbazole).

3-benzothiazol-9H-hexylcarbazole (4)

A mixture of **3** (3.40 g, 13 mmol), 2-aminothiophenol (1.75 g, 14 mmol) in DMSO was kept at 170 °C for 12 h. The reaction mixture was cooled down to room temperature and poured into brine. After the solvents were removed in rotary evaporation, the crude products were recrystallized from ethanol to obtain a yellow crystal 2.74 g. Yield: 62.2%. ¹H NMR (Fig. S5, 400 MHz, CDCl₃) δ (pm): 8.85(s, H), 8.21(t, 2H), 8.09(d, *J* = 8.40 Hz, H), 7.91(d, *J* = 8.00 Hz, H), 7.52–7.41(m, 4H), 7.37(t, H), 7.31(t, H), 4.32(t, 2H), 1.88(m, 2H), 1.39–1.24(m, 6H), 0.86(t, H). FT-IR (Fig. S6, KBr, cm⁻¹): 2952–285(-CH₃, -CH₂-), 1627–1591(structure of carbazole), 3131, 1477–1423, 748–725(benzene), 1129–946(-S-C).

6-benzothiazol-2-yl-9H-hexylcarbazole-3-carbaldehyde (5)

The product was synthesized by the similar procedure for synthesis of **3**, giving a faint yellow powder of the product in 57.2% yield. ¹H NMR (Fig. S7, 400 MHz, CDCl₃) δ (pm): 10.13(s, H), 8.88(s, H), 8.70(s, H), 8.28(d, *J* = 10.00 Hz, H), 8.08(m, 2H), 7.92 (d, *J* = 8.00 Hz, H), 7.52(t, 3H), 7.39(t, H), 4.37(t, 2H), 1.91(t, 2H), 1.37(m, 6H), 0.87(t, 3H). FT-IR (Fig. S8, KBr, cm⁻¹): 2952–2854(-CH₃, -CH₂--), 1627–1596(structure of carbazole), 1682(C=O), 3062, 1479–1426, 759–725(benzene), 1164–1128(-S-C).

3-(6-benzothiazol-2-yl-9H-hexylcarbazole -3-yl)-2-cyano-acylic acid (D3)

To a solution of **5** (0.73 g, 1.9 mmol) in 10 mL acetonitrile was added cyanoacetic acid (0.3 g, 3.5 mmol), dichloromethane and piperidine (0.1 mL). The solution was refluxed for 18 h. After cooled down to room temperature, the solvent was removed by rotary evaporation. The product was obtained by silica gel chromatography (CH_2Cl_2 :MeOH = 10:1 as eluent) as a green solid 0.62 g. Yield: 68.5%. ¹H NMR (Fig. S9, 400 MHz, DMSO-d₆) δ (pm): 13.76(s, H), 9.03(s, H), 8.90(s, H), 8.48(s, H), 8.36(d, J = 4.40 Hz, H), 8.24(d, J = 8.40 Hz, H), 8.15(d, J = 8.00 Hz, H), 8.07(d, J = 8.0J = 4.80 Hz, H), 7.88(m, 2H), 7.55(t, H), 7.45(t, H), 4.50(t, 2H), 1.81(t, 2H), 1.24(m, 6H), 0.80(t, 3H). FT-IR (Fig. S10, KBr, cm⁻¹): 2925-2854(-CH₂, -CH₃), 1710-1631(structure of carbazole), 2212(-C=N), 1710(-C=O), 1430(-OH), 3066, 582-1430, 800-708 (structure of benzene), 1023(C=N), 1203-1159(-S-C). Elemental analysis: Anal. Calcd for C₂₉H₂₅N₃O₂S: C 72.63, H 5.25, N 8.76, S 6.69, Found; C 72.65, H 5.26, N 8.77, S 6.70.

6-iodo-9H-hexylcarbazole-3-carbaldehyde (6)

Amount of **3** (1.40 g, 5 mmol) was added in the flask with 25 mL glacial acetic acid and stirred vigorously till dissolved completely. KI (1.66 g) and KIO₃ (3.21 g) were added in the solution. The mixture was stirred at 70 °C for 3 h. After cooled down to room

temperature and it was washed with mixed solution of 100 mL CH₂Cl₂ and 50 mL H₂O. The extract was washed with NaHSO₃ aqueous solution and adjusted to pH = 8 with ammonia. Then the yellow organic solvents in lower was removed in rotary evaporation, the crude products were recrystallized from ethanol to obtain a yellow power (1.58 g). Yield: 78.2%. ¹H NMR (Fig. S11, 400 MHz, CDCl₃) δ (pm): 10.09(s, H), 8.54(s, H), 8.46(d, *J* = 8.40 Hz, H), 8.01(d, *J* = 8.00 Hz, H), 7.75(d, *J* = 4.00 Hz, H), 7.45(d, *J* = 8.40 Hz, H), 7.25(d, *J* = 8.40 Hz, 2H), 4.28(t, 2H), 1.84(t, 2H), 1.27(m, 6H), 0.96(t, 3H). FT-IR (Fig. S12, KBr, cm⁻¹):1686(-C=O), 3079-2924(-CH₃, -CH₂--), 569(-I), 1623-1588(structure of carbazole).

3-benzothiazole-6-iodo-9H-hexylcarbazole (7)

The product was synthesized according to the procedure for synthesis of **4**, giving a grey powder in 70.8% yield. ¹H NMR (Fig. S13, 400 MHz,CDCl₃) δ (pm): 8.80(s, H), 8.52(s, H), 8.28(d, J = 8.40 Hz, H), 8.12(d, J = 8.00 Hz, H), 7.91(d, J = 4.00 Hz, H), 7.76(d, J = 8.40 Hz, H), 7.51(m, 2H), 7.40(t, H), 7.22(d, J = 8.40 Hz, H), 4.30(t, 2H), 1.66(t, 2H), 1.32(m, 6H), 0.96(t, 3H). FT-IR (Fig. S14, KBr, cm⁻¹): 2925–2853(-CH₃, -CH₂--), 1623–1589(structure of carbazole), 3059, 1470–1435, 797–728(benzene), 1288–1153(-S-C-).

3-(2-carbaidenhyde-thiophene)-6-benzothiazol-9H-hexylcarbazole (8)

To a solution of **7** (0.88 g, 1.8 mmol) and 5-formyl-2-thiophene boric acid (0.32 g, 2 mmol) in the mixture of toluene and ethanol (toluene:ethanol = 3:1, v/v), 2 M aqueous Na₂CO₃ solution (2 mL), and Pd(PPh₃)₄ (10 mg × 4) was added in batches, the reaction mixture was refluxed for 48 h under nitrogen atmosphere. After cooled down to room temperature, the mixture was poured into a saturated solution of ammonium chloride then extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with brine and dried over MgSO₄. After the solvents were evaporated in rotary evaporation, the residue was purified by chromatography on silica gel (petroleum:ethyl acetate = 5:1 as eluent) to give the product as yellow solid (0.40 g), Yield: 45.4%. ¹H NMR (Fig. S15, 400 MHz, CDCl₃) δ (pm): 9.90(s, H), 8.87(s, H), 8.49(d, *J* = 1.60 Hz, H), 8.21(d, *J* = 10.00 Hz, 2H), 8.09(d, *J* = 8.00 Hz, 2H), 7.92(d, *J* = 8.00 Hz, H), 7.78(m, 2H), 7.48(m, 4H), 7.38(t, H), 4.33(t, 2H), 1.90(t, 2H), 1.31(m, 6H), 0.96(t, 3H). FT-IR (Fig. S16, KBr, cm⁻¹): 2952–2852(-CH₃, -CH₂-), 1598(structure of carbazole), 1655(C=O), 3091, 1470–1433, 758(benzene), 797(structure of thiophene).

3-[5-(6-Benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-thiophen-2-yl]-2-cyano-acylic acid (D4)

The product was synthesized similar as the procedure for synthesis of D3, giving a red powder in 65.8% yield. ¹H NMR (Fig. S17, 400 MHz, DMSO-d₆) δ (pm): 9.94(s, H), 9.11(d, J = 8.00 Hz, H), 8.95(d, J = 12.40 Hz, H), 8.50(d, J = 4.40 Hz, H), 8.26(d, J = 8.40 Hz, H), 8.17(d, J = 8.00 Hz, H), 8.07(d, J = 4.80 Hz, 2H), 7.92(t, 2H), 7.84–7.78(m, 2H), 7.57(t, H), 7.47(t, H), 4.50(s, 2H), 1.83–1.80(m, 2H), 1.30–1.22(m, 6H), 0.83(t, 3H). FT-IR (Fig. S18, KBr, cm⁻¹): 2924–2853 (-CH₂, -CH₃), 1579(structure of carbazole), 2213(-C=N), 1707(-C=O), 1430(-OH), 1628, 756–725(=C-H), 1189(-S-C), 797(structure of thiophene). Elemental analysis: Anal. Calcd for C₃₃H₂₇N₃O₂S₂: C 70.56, H 4.84, N 5.70, S 11.42, Found: C 70.59, H 4.82, N 7.51, S 11.41.

Preparation of dye-sensitized electrodes

The working TiO₂ electrode for DSSCs was prepared as follows. F-doped tin oxide (FTO) glass plates were immersed into 40 mM TiCl₄ at 70 °C for 30 min and rinsed by water and ethanol. To prepare TiO₂ paste commercial titania power was ground in a mortar



a:n-C₆H₁₃Br NaH DMF 80°C 3h b:POCl₃ DMF 70°C 2h c:KI KIO₃ CH₃COOH 70°C 3h d: ______NH₂ DMSO 170°C 12h ______SH e: OHC S B_{OH}^{OH} Pd(PPh₃)₄ Na₂CO₃ toluene:ethanol= 3:1 N₂ 70°C 48h

f: HOOC__COOH CH₃CN CH₂Cl₂ piperidine 70°C 18h

Scheme 1. The synthetic route of D3 and D4.



Fig. 1. UV–Vis absorption spectra of D3 and D4 in different solvents (10.0 μ M).

with a small amount of water TiO_2 was evenly coated on the glass surface, then the electrodes coated with TiO_2 pastes were heated under airflow at 450 °C for 30 min. The TiO_2 films were immersed into the dye solution (0.3 M in ethanol) for 24 h. After absorption of the dyes, the electrodes were rinsed with chloroform and acetonitrile. The working and Pt-counter electrodes were assembled into a sealed sandwich solar cell.

Table 1

UV-Vis spectra and fluorescence spectra data of D3 and D4 in different solvents.

Results and discussion

Synthesis and characterization

As shown in Scheme 1, D3 and D4 are 3-benzothiazole carbazole-based derivative molecules with cyanoacetic acid and thiophene cyanoacetic acid, respectively. The carbazole was easily converted to **2** by N-alkylation and **3** was prepared by a Vilsmeier reaction of N-hexylcarbazole with POCl₃ in DMF [25–26]. Synthesis of **4** from **3** (or **7** from **6**) is Phillips Method to transform 2-aminothiophenol to benzothiazole. Treatment of the 5-formyl-2-thiophene boric acid with **7** through Suzuki coupling reaction gave an important intermediate aldehyde **8**. In this reaction, we added Pd(PPh₃)₄ in batches to raises the yield obviously compared to the literature [27]. The reason may be that Pd(PPh₃)₄ is sensitive with the air, light, heat and moisture. The final reaction for D3 and D4 was the condensation of the respective aldehyde with cyanoacetic acid by the Knoevenagel reaction with piperidine as catalyst.

UV-Vis absorption spectral studies

The UV-Vis absorption spectra of the D3 and D4 in several solvents with different polarity are illustrated in Fig. 1. The spectral data are summarized in Table 1. D3 exhibits two absorption bands, a high-energy absorption band at 308-319 nm and a low-energy absorption band at 359-375 nm (except 391 nm in dichloromethane). D4 exhibits three absorption bands, a high-energy absorption band at 319-327 nm, a low-energy absorption band at 396–406 nm (except 431 nm in dichloromethane) and an unconspicuous band 345-349 nm. The high-energy absorption band is attributed to the $\pi - \pi^*$ electron transition of the conjugated system between benzothiazole and cabazole moiety and the low-energy absorption band is attributed to the intramolecular charge transfer (ICT) from the carbazole unit to the cyanoacylic acid units. In addition, D3 and D4 exhibit different maximum absorption wavelengths (Fig. S19). The low-energy absorption band of D4 (400 nm) obviously red-shifted compared with D3 (359 nm), which is ascribed to the incorporating thiophene unit between carbazole moiety and cyanoacylic acid to extend the π -conjugation system while the high-energy absorption band is also red-shifted [28–29]. As the solvent polarity increases the maximum absorption wavelength of D3 (391 to 359 nm) and D4 (431 to 396 nm) blue shifted steming from a polar interaction and/or deprotonation [30].

Compounds	Solvents	UV wavelength $\lambda_U (nm)^a$	Emission wavelength Ex (nm)ª	Excited wavelength Em (nm) ^a	Stokes shift (cm ⁻¹) ^b	Fluorescence quantum yield $(\Phi)^{c}$	Fluorescence lifetime (τ , ns)
D3	Dichloromethane	391,319	391	431	2374	0.057	0.39
	Ethyl acetate	375,312	375	415	2570	0.070	0.59
	Ethanol	371,308	371	422	3257	0.112	0.28
	Acetonitrile	359,313	359	420	4047	0.091	1.05
	Dimethyl formamide	364,312	364	418	4579	0.095	1.06
D4	Dichloromethane	431,347,319	431	484	2541	0.271	2.03
	Ethyl acetate	406,349,322	406	480	3798	0.318	1.03
	Ethanol	404,346,322	404	496	4591	0.239	0.60
	Acetonitrile	400,345,321	400	492	4675	0.358	1.39
	Dimethyl formamide	396,348,327	396	491	4886	0.242	1.65

 a The concentration of solutions is 10.0 μ M.

 $^{\rm b}$ Stokes shift was calculated from 1/Ex – 1/Em.

 $^{c} \Phi_{s} = \Phi_{r} \frac{F_{A}}{F_{r}A_{0}} (\frac{n_{L}}{n_{s}})^{2}$ where *F* is the integration of the emission intensities, n is the index of refraction of the solution, Φ is the fluorescence quantum yield and *A* is the absorbance at the excitation wavelength, the subscripts "*r*" and "s" denote the reference and unknown samples respectively.

The fluorescence spectral studies

The fluorescence spectra of the two compounds were measured in different polar solvents and the spectral data are also collected in Table 1. The emission spectra of D3 and D4 consist of one broad band. As shown in Fig. 2. and Table 1, D3 and D4 display mainly a broad emission band in several solvents owe to overlap of π – π ^{*} transition of their skeletons and π – π ^{*} transition of the ICT from the carbazole unit to the cyanoacylic acid unit. The polarity of the solvent has a slight impact on fluorescence emission wavelength. The fluorescence intensity in dichloromethane, ethyl acetate and ethanol show a decreasing tendency. This may be caused by the different interaction between solvent and dye molecules [31].

In order to further investigate the fluorescence emission properties of D3 and D4, their Stokes shifts and fluorescence quantum yields are studied and summarized in Table 1. Stokes shifts of D3 and D4 become larger with the increase of solvent polarity. It is larger in the case of the polar solvents when the hydrogen bonds or dipol-dipol interactions are most possible [32]. It could be seen that the introduction of thiophene moiety raises the fluorescence quantum yield that might resulted from the elongation of the conjugated bridge length of D4, so the molar absorption coefficient is increased and π electron is more easily excited. The fluorescence spectra have been recorded in different solvents and the fluorescence maximum of these compounds red shift upon increasing



Fig. 2. The normalized fluorescence spectra of D3 and D4 in different solvents (10.0 $\mu M).$

the solvent polarity (fluorescence solvatochromism) which supports the excited state charge transfer character.

The fluorescence decay behaviors of compound D3 and D4 were also studied in several solvents Fig. S19. The fluorescence lifetimes (τ, ns) of D3 and D4 are collected in Table 1. The fluorescence lifetime of D4 is longer than that of D3. On the other hand, the lifetimes of D3 and D4 in polar solvents are longer than in non-polar solvents. With the increase of solvent polarity, the dipole-dipole interaction of molecular in excited state is strengthened, leading to the polarity increase of the excited state and the reduction of the energy of molecular excited state. We can also find that the lifetimes of D3 and D4 in ethanol are clearly shorter than in other solvents because of lots of hydrogen bonds in it. Considering from the application in DSSCs, the lifetimes of D3 and D4 are short. This means that D3 (D4) can facilitate the charge recombination. The facilitation can be interpreted as being that D3 (D4) attracts I_3 by dispersive force and there are spaces for $I_{\overline{3}}$ to be around the dyes [33].

The electrochemical properties

In order to investigate the properties of the D3, D4, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) analysis were performed. The measurements were carried out in CH₃CN solution containing 0.1 M n-Bu₄NClO₄ as supporting electrolyte [34]. The results are shown in Fig. 3 and summarized in Table 2. The CV curves of two molecular remain unchanged under successive oxidation, indicating their excellent stability against electrochemical oxidation. The oxidation potential ($E_{\rm ox}$) corresponds to HOMO while the reduction potential ($E_{\rm red}$) to LUMO. A positive shift of the $E_{\rm HOMO}$ and $E_{\rm LUMO}$ was observed for D3 ($E_{\rm HOMO} = -5.73$ V, $E_{\rm LUMO} = -2.28$ V) vs. D4 ($E_{\rm HOMO} = -5.92$ V, $E_{\rm LUMO} = -2.86$ V), which resulted from introduction of the thiophene moiety.

Frontier molecular orbitals

The time-dependent hybrid density functional theory (TDDFT) calculations were performed using B3LYP/6-31G[•](d, p). B3LYP is a hybrid function modified from the three-parameter exchange–correlation functional of Becke [37]. Table 3 and Fig. 4 present the calculation results of D3 and D4. The results from theoretical calculation revealed that the HOMO of D3 and D4 are localized on main conjugated framework between the carbazole and cyano-acetic acid, and the LUMO are mainly located on the thiophene



Fig. 3. Cyclic voltamograms of D3 and D4 in acetonitrile.

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Compounds	$\lambda_{abs} (nm)^{a}$	$E_{\rm g} \left({\rm V} \right)^{\rm b}$	$E_{\text{onset}(\text{ox})}(V)^{c}$	$E_{\rm HOMO} (\rm V)^{\rm d}$	$E_{\rm LUMO} (V)^{\rm d}$	$E_{\rm ox}$ (V vs. NHE)	$E_{\rm ox} - E_{\rm g}(V {\rm vs. NHE})$
D3	359	3.45	1.09	-5.73	-2.28	2.06	-1.39
D4	405	3.06	1.28	-5.92	-2.86	1.73	-1.33

^a Absorption spectra were measured in acetonitrile.

^b E_g values were calculated from intersect of the normalized absorption and the emission spectra (λ_{abs}): $E_g = 1240/\lambda_{abs}$).

^c The oxidation potentials (vs. NHE) of compounds were measured on 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile using a glass carbon working electrode, a Pt counter electrode and a saturated calomel reference electrode.

^d $E_{\text{HOMO}} = -[E_{\text{onset}(\text{ox})} + 4.4 \text{ eV} + 0.24 \text{ eV}] [35-36], E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}(\text{vs. SCE}).$

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Calculated single-photon-related photophysical properties of D3 and D4.

Compound	Excited state	<i>E</i> (eV)	λ (nm)	f	Composition	Character
D3	1 2	3.3770 3.8789	359.14 313.64	0.2932 0.4276	$HOMO-1 \rightarrow LUMO$ $HOMO \rightarrow LUMO+2$	$\begin{array}{l} \text{ICT} \\ \pi \rightarrow \pi^{^{*}} \end{array}$
D4	1 2 3	2.9884 3.5244 3.9687	400.89 345.79 321.40	0.3368 0.2876 0.5030	$HOMO-1 \rightarrow LUMO$ $HOMO \rightarrow LUMO+1$ $HOMO-1 \rightarrow LUMO+1$	



Fig. 4. The frontier molecular orbitals of the HOMO and LUMO.



Fig. 5. Schematic energy level diagram for a DSSC based on dyes.

cyanoacetic acid units, respectively. Additionally, the results also show that the D4 possess two charge-transition states compared to the D3 because the insertion of thiophene group can enhance the ICT and effective π -electron delocalization. Two transitions of D3 resemble those observed in the experimental linear absorption spectra. The transitions at ca. 359 nm (f = 0.2932) and 313 nm (f = 0.4276) originating from HOMO-1 \rightarrow LUMO and HOMO \rightarrow -LUMO+2 transitions are assigned as the ICT transitions of D3. While the transitions at ca. 400 nm (f = 0.3368), 345 nm (f = 0.2806) 321 nm (f = 0.5030) originating from HOMO--1 \rightarrow LUMO, HOMO \rightarrow LUMO+1 and HOMO-1 \rightarrow LUMO+1 transitions of D4, showed that the distributions of HOMO and LUMO levels are separated in D4, indicating that the HOMO--1 \rightarrow LUMO+1 transition can be ascribed to a π - π * mixed charge-transfer transition.

There is a very important application of D3 and D4 as organic sensitizers of Dye-sensitized solar cells (DSSCs), which emerged as a new generation photovoltaic device and had received considerable attention in recent years because of their high efficiency and low-cost [38-40]. Fig. 5 shows the schematic energy diagram of these dye-sensitized TiO₂ electrodes. To get an efficient charge separation, the LUMO of the dye from where the electron injection occurs has to be sufficiently more negative than the conduction band edge of the TiO_2 (E_{cb}) [41], and the HOMO has to be more positive than the redox potential of I_3^-/I^- [42]. The HOMO levels of D3 and D4 dyes are 2.06, and 1.73 V (vs. NHE), respectively. We considered that the potential levels of the $E_{ox} - E_{g}$ corresponded to the LUMO levels of the dyes. The HOMO levels of the dyes are sufficiently more positive than I_3^-/I^- redox potential value, indicating that the oxidized dyes formed after electron injection to TiO₂ could accept electrons from I[–] ions thermodynamically [41]. From these values, we can find the introduction of thiophene unit into the molecules shift the HOMO levels negatively, which thus decrease the gap between the HOMO level and the redox potential of I_3^-/I^- . This might increase the efficiency of regeneration of the oxidized dye by I⁻ and the overall solar-to-electrical energy conversion efficiency at the same time. These LUMO are sufficiently more negative than the E_{cb} of TiO₂ (-0.5V vs. NHE). The relatively large energy gaps between the LUMO and E_{cb} allow for the addition of the 4-tert-butylpyridine (TBP) to the electrolyte [43], which shift the E_{cb} of the TiO₂ negatively and, consequently, improve the voltage and the total efficiency.

Solar cell performance

All DSSC were fabricated from a TiO₂ film, which consists of a layer of TiO₂ nanoparticle film (TiO₂ P25 21diameter).We compared the *J*–*V* curves of D3 and D4 based divices in Fig. 6 and the results are summarized in Table 4. The devices fabricated from D3 achieved a power conversion efficiency of 0.45%. The device fabricated from D3 showed Voc = 0.66 V, Jsc = 1.33 mA cm⁻² and FF = 0.51, while D4 showed Voc = 0.53 V, Jsc = 2.10 mA cm⁻² and FF = 0.44. It is



Fig. 6. Current–voltage (J–V) curves for DSSC based on D3 and D4 under illumination of 100 mW cm $^{-2}$ AM1.5 simulated solar light.

Table 4

Photovoltaic performances of DSSC based on D3 and D4.

Dye	Voc (V)	Jsc (mA cm ⁻²)	FF	η (%)
D3	0.66	1.33	0.51	0.45
D4	0.54	2.10	0.44	0.50

generally believed that a lower Jsc value is correlated to a lack of effective electron injection and/or fast charge recombination process and a narrower and/or lower absorption spectrum [44].

Conclusion

In this paper, we have designed and synthesized the novel thiophene bridged compound D4, which has much stronger π - π^* electron transition band than its similar compound D3, caused maximum absorption wavelengths red-shifted in UV–Vis absorption spectra and a positive shift of the $E_{\rm ox}$ in CV analysis. In different solvents, stokes shifts for D3 and D4 are larger in polar solvents than in non-polar solvents. By comparing the HOMO and LUMO of D3 and D4 by TDDFT calculations and electrochemical properties study, with the conduction band edge of TiO₂ and I₃/I⁻ redox potential, we presume that D3 and D4 are suitable materials for DSSCs. From the solar cell performance, the D4 which contain thiophene unit shows better photovoltaic properties than D3 in DSSCs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.06.159.

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