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



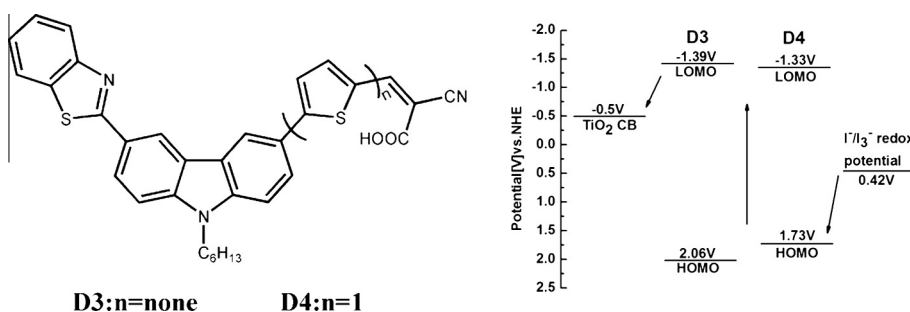
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HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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ABSTRACT

Two carbazole-based dye molecules: 3-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-2-cyano-acrylic acid (D3) and 3-[5-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-thiophen-2-yl]-2-cyano-acrylic 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 ($E_{\text{HOMO}} = 2.06 \text{ V}$, $E_{\text{LUMO}} = -1.39 \text{ V}$ vs. NHE) and D4 ($E_{\text{HOMO}} = 1.73 \text{ V}$, $E_{\text{LUMO}} = -1.33 \text{ V}$ 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 cyanoacrylic 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 TiO₂ 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 I₃⁻/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-acrylic acid (D3) and 3-[5-(6-benzothiazol-2-yl-9H-hexylcarbazole-3-yl)-thiophen-2-yl]-2-cyano-acrylic acid (D4), which were both substituted with benzothiazole 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) 1-bromohexane 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 (ppm): 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 × 50 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 (ppm): 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 (ppm): 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 (ppm): 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-acrylic 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 (CH₂Cl₂:MeOH = 10:1 as eluent) as a green solid 0.62 g. Yield: 68.5%. ¹H NMR (Fig. S9, 400 MHz, DMSO-d₆) δ (ppm): 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* = 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

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