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The synthesis and photoluminescence characteristics of novel 4-aryl substituted thiophene derivatives with bis-diarylacrylonitrile unit

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ABSTRACT

(Z)-2-(4-Bromophenyl)-3-(4-(5-((Z)-2-cyano-2-phenylvinyl)thiophen-3-yl)-phenyl)acrylonitrile was synthesized by (Z)-3-(4-(4-formylphenyl)-thiophen-2-yl)-2-phenylacrylonitrile and 2-(4-bromophenyl) acetonitrile through a base catalyzed condensation reaction, and then reacted with various aryl boronic acids under the catalyzing of $Pd(PPh_3)_4$ to afford a series of novel 4-aryl substituted thiophene derivatives with bis-diarylacrylonitrile unit. The structures of the products were characterized using FTIR, ^1H NMR, ^{13}C NMR, and HRMS. The UV–vis absorption and photoluminescent spectra of these derivatives were investigated. These compounds emit 450–510 nm green fluorescence in the solid state and 446–491 nm emission in CH_2Cl_2 solution under UV irradiation. Analysis revealed good thermal stability with a decomposition temperature ranging from 301 to 378 °C.

1. Introduction

As one of the most promising fields in the past few decades, Organic light-emitting diodes (OLEDs) attracted considerable researches to develop different materials and various devices [1–4]. Due to their excellent properties such as light weight, self emitting, wide view angle and flexibility [5–7], OLEDs have significant applications in replacing cathode ray tubes (CRTs) or liquid crystal displays (LCDs) [8,9]. Among all these OLED materials, thiophene-based materials have shown to be one of the most prospective functional ones [10–12], because of their intrinsic electron-rich nature, excellent environmental and thermal stabilities, special optical and electrical properties, and the easy manipulation of their properties by introducing functional substituents at different positions [11,13].

Thiophene derivatives were also widely used in dyes and pigments [14–16] due to their interesting optical properties [12,15] and electron-donating functions [15]. α,β-acrylonitriles derivatives have important uses as organic light-emitting materials [17,18]. They are also versatile intermediates in the synthesis of various compounds, such as perfumes, Vitamin A, pigments [19,20] and organic dyes [21–23].

Based on the outstanding properties of thiophene and α,β-diarylacrylonitriles derivatives, as well as our previous studies on organic light-emitting device materials [24–27], we were interested in the preparation of a series of novel functionalistic aryl substituted thiophene derivatives for potential applications in dyes, pigments and as hole-transporting emitters in organic light-emitting devices [24,28–30]. In this paper, we report the synthesis and photophysical properties of novel fluorescent aryl substituted thiophene derivatives with bis-diarylacrylonitrile unit. The structures of these compounds were characterized by FTIR, ^1H NMR, ^{13}C NMR, and HRMS. The UV–vis absorption (UV–vis) and photoluminescent spectrum (PL) were investigated. And the general properties such as solubility and thermal properties were reported.

2. Experimental

2.1. Materials

Palladium, aryl boronic acids, Na_2CO_3, dimethoxyethane were purchased from Aldrich Chemical Co. Sodium tert-butoxide was purchased from Alfa-Aesar and stored in a vacuum atmospheres glove box under nitrogen. All chemicals were used as supplied.

2.2. Instruments and measurements

All melting points were determined with a WRS-1A melting point apparatus and were uncorrected. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TGA/SDTA 851e. Nuclear

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magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were run on a Bruker AV-400 NMR or a Bruker DMX-500 NMR spectrometer in $CDCl_3$. IR spectra were recorded in KBr on a Nicolet NEXUS 470 FTIR spectrophotometer. UV–vis spectra were taken using a Hitachi U-3300 model, while a Hitachi F-4500 fluorescence spectrophotometer was used to take the PL spectra. All the mass spectroscopy data of the products were collected using a gas chromatography-high resolution time of flight mass spectrometer made by Waters Corporation of US (GCT Premier).

2.3. Synthesis

2.3.1. Synthesis of compound (**1**)

A solution of 4-bromothiophene-2-carbaldehyde (0.191 g, 1.00 mmol), benzyl cyanide (0.128 g, 1.10 mmol) and sodium methoxide (0.54 mg, 0.01 mmol) in 10 mL EtOH was stirred for 4 h at room temperature in a 100 mL round bottom flask, and then filtered. The precipitate was washed with cold EtOH.

2.3.2. Synthesis of compound (**2a**)

To a 50 ml sidearm flask was added compound **1** (0.291 g, 1.00 mmol), (4-formylphenyl) boronic acid (0.157 g, 1.10 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol) and sodium carbonate (0.233 g, 2.20 mmol), EtOH (3.0 mL), dimethoxyethane (7.5 mL),H_2O (2.0 mL) was injected into the flask from a syringe. The reaction mixture was heated and stirred at 85 °C under nitrogen for 8 h until the reaction was completed. The reaction mixture was then cooled to room temperature, filtered through a mixture of celite and silica gel pad and washed with dichloromethane. The filtrate was washed with water and then dried by $MgSO_4$. Concentration of the filtrate on a rotary evaporator followed by washing of the solid material with ethanol afforded the desired crude product. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether(1/1) as eluents.

*2.3.2.1. (Z)-3-(4-(4-formylphenyl)thiophen-2-yl)-2-phenylacrylonitrile (**2a**).* Pale yellow solid. Yield: 90%. M.p. 186 °C. FTIR (KBr pellet, cm^{-1}): 3093, 2822, 2718, 2209, 1696, 1605, 1212, 1162, 822, 763. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 10.03 (s, 1H), 7.99(s, 1H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.77–7.75 (m, 3H), 7.67–7.65 (m, 3H), 7.47–7.40 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$):δ_c: 191.58, 141.50, 140.32, 139.06, 135.46, 133.56, 133.50, 130.51, 130.41, 129.30, 129.19, 126.82, 126.39, 125.77, 117.94, 109.46. HRMS (EI): Calcd for $C_{20}H_{13}NOS$: 315.0718. Found: 315.0720.

2.3.3. General procedure for the synthesis of compounds (**3a**–**3g**)

A solution of compound **2a** (0.299 g, 1 mmol), aromatic acetonitrile halides (1.10 mmol) and sodium methoxide (0.54 mg, 0.01 mmol) in 10 mL EtOH was stirred for 4–8 h at 60 °C in a 25 mL round bottom flask, and then filtered. The precipitate was washed with water till PH = 7, and then purified by column chromatography on silica gel using ether aceter/dichloromethane/petroleum ether (1/0.2/2) as eluents.

*2.3.3.1. (Z)-3-(4-(4-((E)-2-cyano-2-(3,4-dimethoxyphenyl)vinyl)phenyl) thiophen-2-yl)-2-phenylacrylonitrile (**3a**).* Yellow solid. Yield: 88%. M.p. 196–198 °C. FTIR (KBr pellet, cm^{-1}): 3084, 3057, 3030, 2964, 2925, 2834, 2209, 1605, 1514, 1254, 1144, 1022, 825, 766. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (s, 1H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.72–7.66 (m, 6H), 7.47–7.37 (m, 4H), 7.29–7.26 (m, 1H), 7.16 (s, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 150.15, 149.31, 141.81, 139.42, 138.80, 136.12, 133.70, 133.63, 133.19, 130.49, 129.80, 129.66, 129.15, 127.21, 126.63, 125.74, 125.48, 119.07, 118.23, 118.01, 111.30, 111.24, 109.02, 108.73, 56.06, 56.04. HRMS (EI): Calcd for $C_{30}H_{22}N_2O_2S$: 474.1402. Found: 474.1409.

*2.3.3.2. (Z)-3-(4-(4-((Z)-2-cyano-2-(naphthalen-1-yl)vinyl)phenyl) thio-phen-2-yl)-2-phenylacrylonitrile (**3b**).* Yellow solid. Yield: 84%. M.p. 208–210 °C. FTIR (KBr pellet, cm^{-1}): 3104, 3057, 3012, 2920, 2209, 1569, 1444, 1186, 909, 775.^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.20 (d, $J = 8.8$ Hz, 1H), 8.04–8.00 (m, 3H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.8$ Hz, 3H), 7.68 (d, $J = 7.6$ Hz, 3H), 7.62–7.51 (m, 4H), 7.48–7.36 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 146.99, 141.79, 138.90, 136.80, 133.85, 133.75, 133.68, 133.49, 132.93, 130.75, 130.58, 129.98, 129.90, 129.22, 129.18, 128.77, 127.34, 127.10, 126.80, 126.52, 125.78, 125.68, 125.40, 124.53, 118.68, 118.00, 109.79, 109.18. HRMS (EI): Calcd for $C_{32}H_{20}N_2S$: 464.1347. Found: 464.1349.

*2.3.3.3. (Z)-2-(4-bromophenyl)-3-(4-(5-((Z)-2-cyano-2-phenylvinyl) thio-phen-3-yl)-phenyl)acrylonitrile (**3c**).* Yellow solid. Yield: 85%. M.p. 182–183 °C. FTIR (KBr pellet, cm^{-1}): 3102, 3068, 3051, 2926, 2212, 1592, 1180, 1070, 826, 757. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (d, $J = 4.8$ Hz, 2H), 7.94 (s, 1H), 7.74 (s, 1H), 7.72–7.66 (m, 5H), 7.60–7.52 (m, 5H), 7.48–7.40 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 141.69, 141.63, 138.90, 136.76, 133.62, 133.36, 132.72, 132.27, 130.38, 130.09, 129.23, 129.18, 127.44, 127.19, 126.75, 125.76, 125.67, 123.50, 117.99, 117.70, 110.36, 109.20. HRMS (EI): Calcd for $C_{28}H_{17}BrN_2S$: 492.0296. Found: 492.0289.

*2.3.3.4. (Z)-3-(4-(4-((Z)-2-cyano-2-phenylvinyl)phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**3d**).* Yellow solid. Yield: 87%. M.p. 174–175 °C. FTIR (KBr pellet, cm^{-1}): 3102, 3054, 3030, 2926, 2212, 1589, 1450, 1180, 897, 832, 770. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 (d, $J = 8.4$ Hz, 3H), 7.71–7.65 (m, 8H), 7.52 (s, 1H), 7.47–7.36 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 141.60, 141.18, 138.73, 136.32, 134.26, 133.60, 133.51, 132.89, 130.44, 129.92, 129.17, 129.08, 129.02, 126.55, 125.86, 125.64, 125.52, 118.02, 117.92, 111.31, 108.90. HRMS (EI): Calcd for $C_{28}H_{18}N_2S$: 414.1191. Found: 414.1194.

*2.3.3.5. (Z)-2-(4-chlorophenyl)-3-(4-(5-((Z)-2-cyano-2-phenylvinyl) thio-phen-3-yl)phenyl)acrylonitrile (**3e**).* Yellow solid. Yield: 83%. M.p.175 °C. FTIR (KBr pellet, cm^{-1}): 3102, 3051, 3027, 2206, 1596, 1486, 1403, 1090, 832, 757. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (d, $J = 5.2$ Hz, 2H), 7.94 (s, 1H), 7.75–7.58 (m, 8H), 7.51 (s, 1H), 7.46–7.41 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 141.78, 141.62, 138.93, 136.81, 135.35, 133.69, 133.65, 132.96, 132.78, 130.38, 130.09, 129.33, 129.19, 127.23, 126.99, 126.79, 125.80, 125.66, 117.98, 117.75, 110.41, 109.29. HRMS (EI): Calcd for $C_{28}H_{17}ClN_2S$: 448.0801. Found: 448.0799.

*2.3.3.6. (Z)-3-(4-(4-((Z)-2-cyano-2-(p-tolyl)vinyl)phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**3f**).* Yellow solid. Yield: 90%. M.p. 156 °C. FTIR (KBr pellet, cm^{-1}): 3084, 3054, 3024, 2920, 2209, 1587, 1186, 894, 831, 757. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (d, $J = 4.4$ Hz, 2H), 7.94 (s, 1H), 7.74 (s, 1H), 7.71–7.67 (m, 5H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.51 (s, 1H), 7.48–7.40 (m, 3H), 7.26 (d, $J = 5.2$ Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 141.71, 140.18, 139.47, 138.77, 133.69, 133.58, 133.10, 131.49, 130.55, 129.88, 129.82, 129.76, 129.14, 126.59, 125.79, 125.70, 125.57, 125.51, 118.18, 117.98, 111.34, 108.91, 21.23. HRMS (EI): Calcd for $C_{29}H_{20}N_2S$: 428.1347. Found: 428.1343.

*2.3.3.7. (Z)-3-(4-(4-((Z)-2-cyano-2-(4-methoxyphenyl)vinyl)phenyl) thio-phen-2-yl)-2-phenylacrylonitrile (**3g**).* Yellow solid. Yield: 84%. M.p. 160 °C. FTIR (KBr pellet, cm^{-1}): 3104, 3030, 2968, 2931, 2834, 2209, 1605, 1512, 1294, 1181, 1031, 829, 760.^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.70–7.60 (m, 8H), 7.46–7.38 (m, 4H), 6.95 (d, $J = 8.8$ Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 160.48, 141.82, 139.14, 138.78, 136.04, 133.74, 133.64, 133.27, 130.57, 129.76, 129.15, 127.30, 126.86, 126.62, 125.74, 125.46, 118.23, 118.00, 114.54, 114.45, 111.07, 108.98, 55.44. HRMS (EI): Calcd for $C_{29}H_{20}N_2OS$: 444.1296. Found: 444.1299.

2.3.4. General procedure for the synthesis of compounds (**4a**–**4h**)

To a 50 ml sidearm flask was added compound **3c** (0.246 g, 0.50 mmol), aryl boronic acids (0.55 mmol), $Pd(PPh_3)_4$ (0.160 g, 0.05 mmol) and sodium carbonate (0.12 g, 1.10 mmol), EtOH (5.0 mL), dimethoxyethane (15 mL), H_2O (5.0 mL) was injected into the flask from a syringe. The reaction mixture was heated and stirred at 85 °C under nitrogen for an appropriate time until the reaction was completed. The reaction mixture was then cooled to room temperature, filtered through a mixture of celite and silica gel pad and washed with dichloromethane. The filtrate was washed with water and then dried by $MgSO_4$. Concentration of the filtrate on a rotary evaporator followed by washing of the solid material with ethanol afforded the desired crude product. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (3/2) as eluents.

*2.3.4.1. 3-(4-(4-((Z)-2-cyano-2-(4-(naphthalen-1-yl)phenyl)vinyl) phenyl) thiophen-2-yl)-2-phenylacrylonitrile (**4a**).* Bright yellow solid. Yield: 87%. M.p. 203 °C. FTIR (KBr pellet, cm^{-1}):3057, 3030, 2968, 2926, 2209, 1584, 1186, 802, 757. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 8.01–7.98 (m, 2H), 7.94–7.88 (m, 3H), 7.82 (d, J = 8.0 Hz, 2H), 7.74–7.66 (m, 5H), 7.64 (s, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.56–7.38 (m, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ_c: 141.88, 141.77, 141.20, 139.03, 138.85, 136.55, 133.81, 133.72, 133.64, 133.34, 133.05, 131.33, 130.77, 130.52, 130.05, 129.18, 129.15, 128.41, 128.12, 126.95, 126.74, 126.30, 125.94, 125.90, 125.75, 125.64, 125.62, 125.38, 118.11, 117.99, 111.19, 109.10. HRMS (EI): Calcd for $C_{38}H_{24}N_2S$: 540.1660. Found: 540.1661.

*2.3.4.2. (Z)-3-(4-(4-((Z)-2-cyano-2-(4-(naphthalen-2-yl)phenyl)vinyl) phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**4b**).* Bright yellow solid. Yield: 82%. M.p. 224–225 °C. FTIR (KBr pellet, cm^{-1}): 3090, 3051, 3033, 2923, 2212, 1652, 1584, 1498, 1450, 1182, 900, 813. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 8.10 (s, 1H), 8.01 (d, J = 9.0 Hz, 2H), 7.96–7.88 (m, 4H), 7.83 (s, 3H), 7.82–7.73 (m, 4H), 7.69 (d, J = 7.5 Hz, 2H), 7.64 (s, 1H), 7.54–7.41 (m, 7H). ^{13}C NMR (500 MHz, $CDCl_3$): δ_c: 141.88, 141.02, 138.91, 137.25, 133.79, 133.66, 133.41, 133.14, 132.90, 129.47, 129.25, 130.56, 130.10, 129.21, 128.71, 128.31, 128.02, 127.98, 127.72, 126.80, 126.59, 126.55, 126.51, 126.32, 125.95, 125.81, 125.77, 125.65, 125.18, 125.15, 111.12, 109.22. HRMS (EI): Calcd for $C_{38}H_{24}N_2S$: 540.1660. Found: 540.1663.

*2.3.4.3. (Z)-2-([1,1′-biphenyl]-4-yl)-3-(4-(5-((Z)-2-cyano-2-phenyl vinyl) thiophen-3-yl)phenyl)acrylonitrile (**4c**).* Bright yellow solid. Yield: 87%. M.p.173 °C. FTIR (KBr pellet, cm^{-1}): 3051, 3029, 2216, 1589, 1486, 1450, 1413, 1181, 897, 836, 764. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.98 (d, J = 6.8 Hz, 3H), 7.77 (d, J = 8.0 Hz, 2H), 7.73(d, J = 8.0 Hz, 2H), 7.70–7.67 (m, 6H), 7.63 (d, J = 7.6 Hz, 2H), 7.58 (s, 1H), 7.49–7.43 (m, 4H), 7.40–7.37 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 141.99, 141.72, 140.84, 139.87, 138.87, 136.42, 133.70, 133.64, 133.22, 133.03, 130.55, 130.09, 129.20, 129.00, 127.92, 127.67, 127.04, 126.68, 126.38, 126.16, 125.78, 125.65, 118.16, 118.08, 110.99,109.05. HRMS (EI): Calcd for $C_{34}H_{22}N_2S$: 490.1504. Found: 490.1503.

*2.3.4.4. (Z)-3-(4-(4-((Z)-2-cyano-2-(4′-methyl-[1,1′-biphenyl]-4-yl) vinyl) phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**4d**).* Bright yellow solid. Yield: 89%. M.p. 220 °C. FTIR (KBr pellet, cm^{-1}): 3102, 3035, 2968, 2929, 2834, 2210, 1605, 1588, 1497, 1253, 1179, 897, 822, 756. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.99–7.98 (m, 3H), 7.76–7.73 (m, 4H), 7.71 (s, 1H), 7.68–7.64 (m, 5H), 7.59–7.56 (m, 3H), 7.48–7.40 (m, 3H), 7.01 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 159.62, 141.85, 141.70, 140.61, 138.85, 136.47, 133.75, 133.69, 133.15, 132.64, 132.38, 130.54, 130.02, 129.20, 129.17, 128.10, 127.17, 126.74, 126.37, 125.78, 125.58, 118.08, 118.00, 114.39, 111.25, 109.15, 55.40. HRMS (EI): Calcd for $C_{35}H_{24}N_2S$: 504.1660. Found: 504.1558.

*2.3.4.5. (Z)-2-(4′-chloro-[1,1′-biphenyl]-4-yl)-3-(4-(5-((Z)-2-cyano-2-phenylvinyl)-thiophen-3-yl)-phenyl)acrylonitrile (**4e**).* Bright yellow solid. Yield: 86%. M.p.197 °C. FTIR (KBr pellet, cm^{-1}): 3087, 3060, 3030, 2923, 2849, 2206, 1587, 1483, 1182, 1090, 998, 814, 757. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 7.99 (d, J = 7.0 HZ, 3H), 7.78–7.75 (m, 3H), 7.73 (d, J = 8.5 Hz, 2H), 7.68–7.66 (m, 4H), 7.64 (s, 1H), 7.60 (s, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.48–7.43 (m, 4H), 7.42–7.39 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ_c: 141.80, 141.14, 140.79, 138.89, 138.35, 136.64, 134.03, 133.69, 133.67, 133.63, 132.99, 130.44, 130.08, 129.22, 129.17, 129.12, 128.26, 127.53, 126.77, 126.48, 125.78, 125.62, 117.97, 110.99, 109.22. HRMS (EI): Calcd for $C_{34}H_{21}ClN_2S$: 524.1114. Found: 524.1114.

*2.3.4.6. (Z)-3-(4-(4-((Z)-2-cyano-2-(4′-methoxy-[1,1′-biphenyl]-4-yl) vinyl) phenyl)-thiophen-2-yl)-2-phenylacrylonitrile (**4f**).* Bright yellow solid. Yield: 87%. M.p.197–198 °C. FTIR (KBr pellet, cm^{-1}): 3102, 3035, 2968, 2929, 2834, 2210, 1605, 1588, 1497, 1253, 1179, 897, 822, 756. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.99–7.98 (m, 3H), 7.76–7.43 (m, 4H), 7.71 (s, 1H), 7.68–7.64 (m, 5H), 7.59–7.56 (m, 3H), 7.48–7.40 (m, 3H), 7.01 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ_c: 159.62, 141.85, 141.70, 140.61, 138.85, 136.47, 133.75, 133.69, 133.15, 132.64, 132.38, 130.54, 130.02, 129.20, 129.17, 128.10, 127.17, 126.74, 126.37, 126.37, 125.78, 125.58, 118.08, 118.00, 114.39, 111.25, 109.15, 55.40. HRMS (EI): Calcd for $C_{35}H_{24}N_2OS$: 520.1609. Found: 520.1609.

*2.3.4.7. (Z)-3-(4-(4-((Z)-2-cyano-2-(4′-vinyl-[1,1′-biphenyl]-4-yl) vinyl) phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**4g**).* Bright yellow solid. Yield: 81%. M.p.194–196 °C. FTIR (KBr pellet, cm^{-1}): 3084, 3030, 2923, 2209, 1587, 1495, 1186, 998, 900, 829, 757. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 8.00 (s, 1H), 7.99 (d, J = 3.0 Hz, 2H), 7.79–7.76 (m, 3H), 7.73 (d, J = 8.5 Hz, 2H), 7.71–7.68 (m, 5H), 7.62–7.60 (m, 3H), 7.52 (d, J = 8.0 Hz, 2H), 7.48–7.45 (m, 2H), 7.42–7.39 (m, 1H), 6.78 (dd, J = 11.0 Hz, J = 10.5 Hz, 1H), 5.83 (d, J = 18.0 Hz, 1H), 5.31(d, J = 11.0 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ_c: 141.83, 141.55, 140.93, 139.19, 138.87, 137.19, 136.55, 136.23, 133.74, 133.68, 133.32, 133.08, 130.52, 130.06, 129.21, 129.17, 127.47, 127.11, 126.79, 126.75, 126.40, 125.77, 125.62, 118.03, 117.99, 114.34, 111.14, 109.16. HRMS (EI): Calcd for $C_{36}H_{24}N_2S$: 516.1660. Found: 516.1663.

*2.3.4.8. (Z)-3-(4-(4-((Z)-2-cyano-2-(3′,5′-dimethyl-[1,1′-biphenyl]-4-yl) vinyl)phenyl)thiophen-2-yl)-2-phenylacrylonitrile (**4h**).* Bright yellow solid. Yield: 89%. M.p. 185 °C. FTIR (KBr pellet, cm^{-1}): 3026, 2915, 2212, 1604, 1588, 1182, 897, 832, 760, 694. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 (d, J = 8.4 Hz, 3H), 7.72–7.62 (m, 10H), 7.53 (s, 1H), 7.45–7.38 (m, 3H), 7.22 (s, 2H), 7.02 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 142.30, 141.77, 140.72, 139.88, 138.84, 138.48, 136.42, 133.70, 133.65, 133.08, 133.02, 130.52, 129.66, 129.54, 129.16, 127.67, 126.68, 126.49, 126.24, 125.76, 125.58, 124.92, 118.08, 118.00, 111.15, 109.08, 21.42. HRMS (EI): Calcd for $C_{36}H_{26}N_2S$: 518.1817. Found: 518.1820.

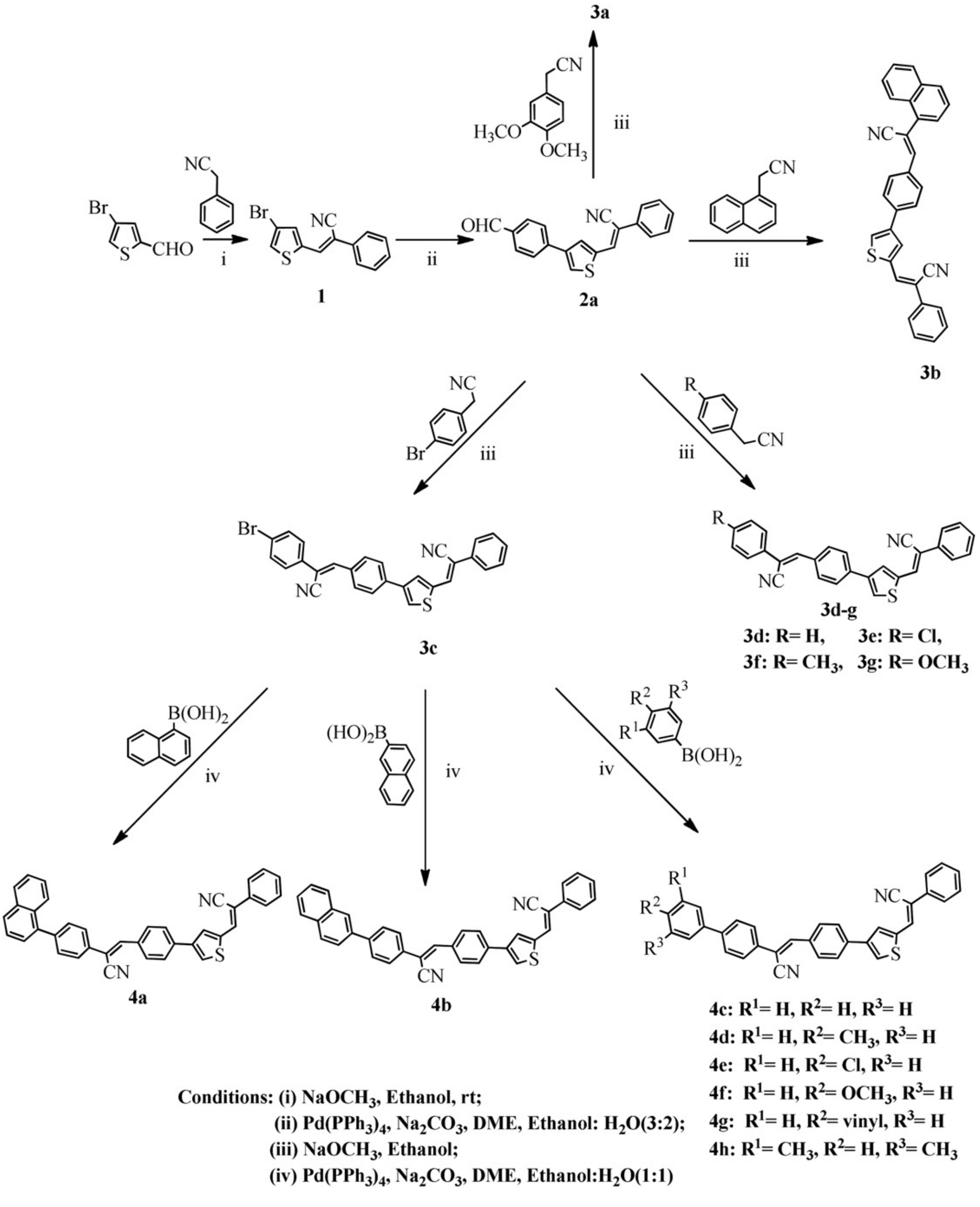
3. Results and discussion

3.1. Synthesis

The target compounds (**3a**–**3g**, **4a**–**4h**) were synthesized through a four-step procedure. The specific synthesis procedure was shown in Scheme 1. Compound **1** was prepared through a base catalyzed condensation reaction of 4-bromothiophene-2-carbaldehyde and benzyl cyanide, and then reacted with (4-formylphenyl)-boronic under the catalysis of $Pd(PPh_3)_4$ to get compound **2a**. Compound (**3a**–**3g**) was then prepared using base catalyzed reaction of compound **2a** and various benzyl cyanide. We then used compound **3c**, via palladium-catalyzed cross-coupling reaction, to prepare a series of novel fluorescent aryl-substituted thiophene derivatives (**4a**–**4h**) with longer conjugated chain.

In this paper, the Suzuki coupling reaction was used twice to prepare the target compounds with longer conjugated chain. The Suzuki cross-coupling reaction has received much attention due to its versatility in the C—C bond formation and construction of biaryl skeleton [31–34]. In this paper, we used $Pd(PPh_3)_4$ as catalyst to prepare compounds (**4a**–**4g**), Na_2CO_3 was used as the base and the solvent system was a mixture of Ethylene glycol dimethyl ether, EtOH and H_2O. The ligand-free catalyst was particularly efficient in this system, which helped to achieve satisfying yields between 81 and 90%. The specific yields are shown in Table 1.

The thermal properties of **3a**–**3g** and **4a**–**4h** were investigated by TGA. The decomposition temperature curves show thermal stability up to 301–378 °C (Table 1), which indicates these compounds may have applications as materials. Compounds **4a**–**4h** have a significant thermal stability increase compared to **3a**–**3g**, which indicates the incorporation of an aryl group enhances the thermal properties. Some representative data have been shown in Fig. 1.



Scheme 1. Synthesis of compounds **3a**–**3g** and **4a**–**4h**.

Table 1
Yields and thermal properties of compounds (**3a**–**3g**) and (**4a**–**4h**).

Entry	Yield [%]	T_m[a] [°C]	T_D[b] [°C]
3a	88	196	324
3b	84	208	353
3c	85	182	322
3d	87	174	302
3e	83	175	321
3f	90	156	313
3g	84	160	350
4a	87	203	354
4b	82	224	351
4c	87	173	378
4d	89	220	345
4e	86	197	328
4f	87	197–198	370
4g	81	194	378
4h	89	185	361

[a] Melting points of compounds **3a**–**3g** and **4a**–**4h**.
[b] Decomposition temperature of compounds **3a**–**3g** and **4a**–**4h**.

3.2. Photophysical properties

In order to investigate their photophysical properties, the UV and PL spectra of compounds (**3a**–**3g**, **4a**–**4h**) in CH_2Cl_2, THF and solid state were recorded. The spectrum data are summarized in Tables 2 and 3, respectively.

The UV–vis absorption spectra shows similar absorption behavior between compounds (**3a**–**3g**, **4a**–**4h**). The absorption spectra of **3a**–**3g**, **4a**–**4h** in CH_2Cl_2 solution are shown in Fig. 2. Each of them reveals a common low-energy broad band at 300–400 nm assigned to the $\pi-\pi^*$ transitions of the compounds. A change of solvent from CH_2Cl_2 to THF resulted in a little blue shift (7–18 nm) of the absorption maximum (Table 2). Some representative spectra are shown in Fig. 3.

Photoluminescent spectra of the compounds (**3a**–**3g**, **4a**–**4g**) were also recorded in CH_2Cl_2 solution. For the emission spectra in CH_2Cl_2 solution, the PL spectra of compounds **3a**–**3g** and **4a**–**4h** are summarized in Tables 2 and 3. The maximal emission peaks of **3a**–**3g** and **4a**–**4h** are mainly located at about 416–457 nm and 446–491 nm respectively. All compounds yield blue or green emissions in CH_2Cl_2 solution at room temperature. The Photoluminescent spectra of the compounds **4a**–**4h** in THF solution were recorded and summarized in Table 3 as well. A change of the

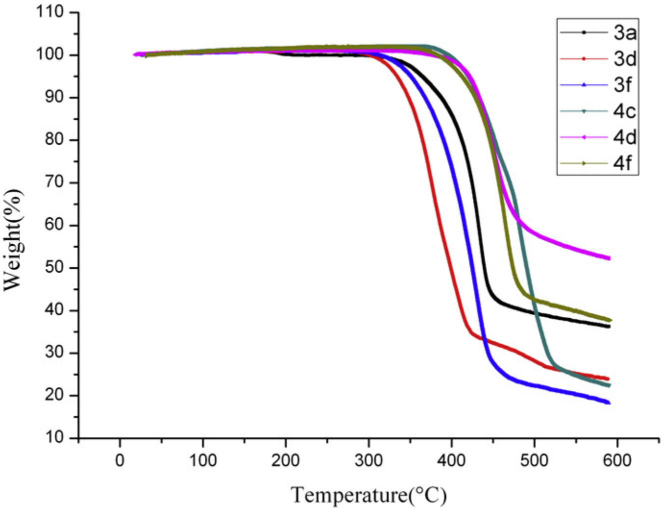


Fig. 1. The TGA spectrum of compounds (**3a**, **3d**, **3f**, **4c**, **4d**, **4f**).

Table 2
Photophysical properties of compounds (**3a**–**3g**).

Entry	CH_2Cl_2 λ_{abs} [nm]	CH_2Cl_2 λ_{em} [nm]	Solid λ_{em} [nm]
3a	369	457	489
3b	357	445	496
3c	344	435	480
3d	357	418	468
3e	361	425	463
3f	360	426	492
3g	362	437	476

Table 3
Photophysical properties of compounds (**4a**–**4h**).

Entry	CH_2Cl_2 λ_{abs} [nm]	CH_2Cl_2 λ_{em} [nm]	THF λ_{abs} [nm]	THF λ_{em} [nm]	Solid λ_{em} [nm]
4a	364	449	355	443	489
4b	361	491	349	448	489
4c	366	446	353	442	483
4d	368	451	350	442	495
4e	366	447	351	444	475
4f	369	462	353	451	484
4g	366	453	351	443	508
4h	370	446	363	444	484

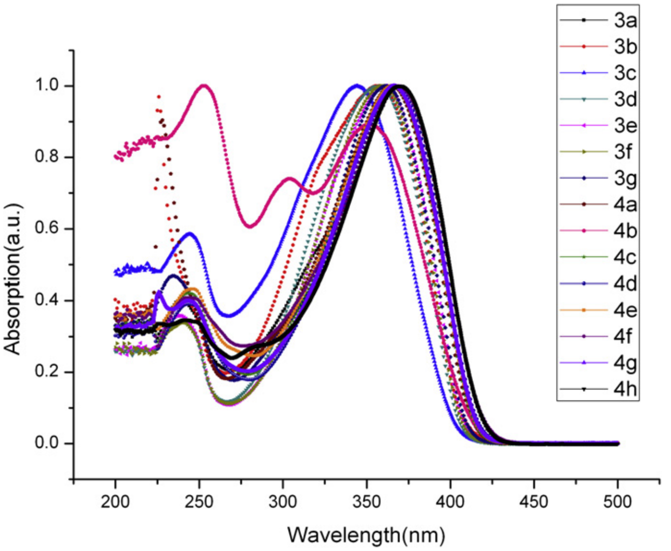


Fig. 2. Absorption spectra of compounds **3a**–**3g**, **4a**–**4h** in CH_2Cl_2 solution.

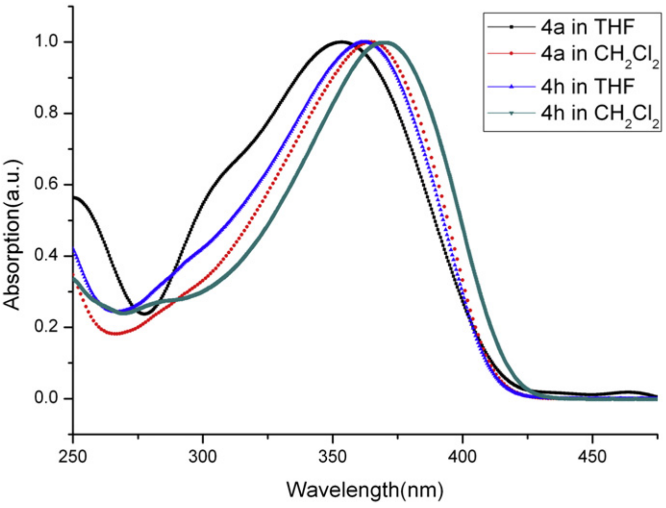


Fig. 3. Absorption spectra of compounds **4a** and **4h** in different solutions.

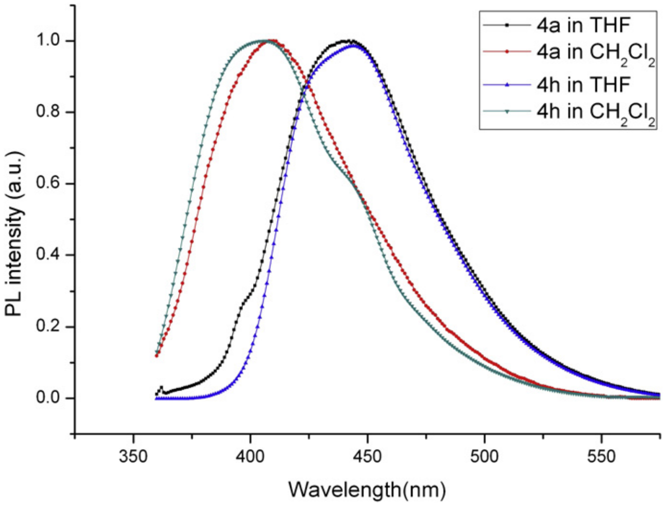


Fig. 4. PL spectra of compounds **4a** and **4h** in different solutions.

solvent from CH_2Cl_2 to THF resulted in a 2–43 nm red shift of the emission maximum, which indicates that the polarity of the solvent plays an important role on the photophysical properties in such strong donor–acceptor systems. Some representative spectra are shown in Fig. 4.

Emission spectra of compounds **3a**–**3g** and **4a**–**4h** in the solid state were determined with an excitation wavelength of 360 nm, the results are shown in Tables 2 and 3 and Fig. 5. All of the compounds exhibit green emission with a maximum peak at 450–510 nm. The emission peaks of series 4 (**4a**–**4h**) in the solid state show a red shift compared to compound **3d** which is attributed to the introduction of a phenyl group.

In order to study the effects on photophysical properties after the introduction of a phenyl group, comparisons between series **3** and series **4** were made. Fig. 6 exhibit the emission spectra of compounds **3d**, **3f**, **4c**, **4d** in CH_2Cl_2. The only difference between **3d**–**4c**, and **3f**–**4d** is the introduction of a biphenyl group which extend the conjugated pathway. It can be found that PL spectra of **4c**, **4d** in CH_2Cl_2 solution and in the solid state are all red shifted relative to those of **3d**, **3f**. Similar results can also be found between **3e**–**4e**, and **3g**–**4f**. The red shifts in these compounds result from the extension of the conjugated length.

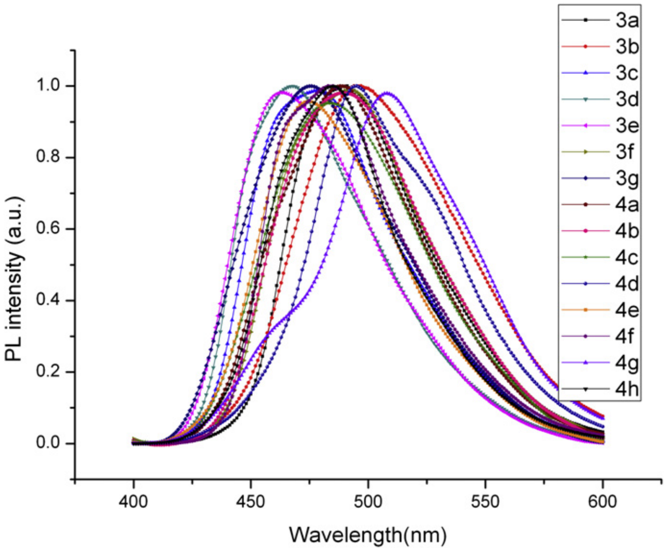


Fig. 5. PL spectra of compounds (**3a**–**g**, **4a**–**h**) in solid state.

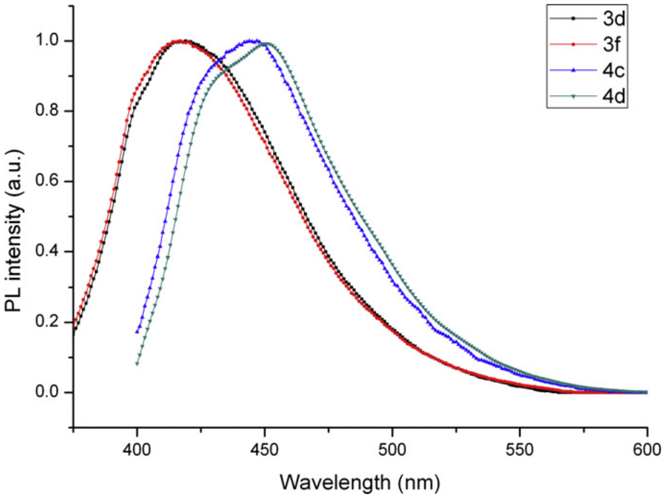


Fig. 6. PL spectra of compounds (**3d**, **3f**, **4c**, **4d**) in CH_2Cl_2 solution.

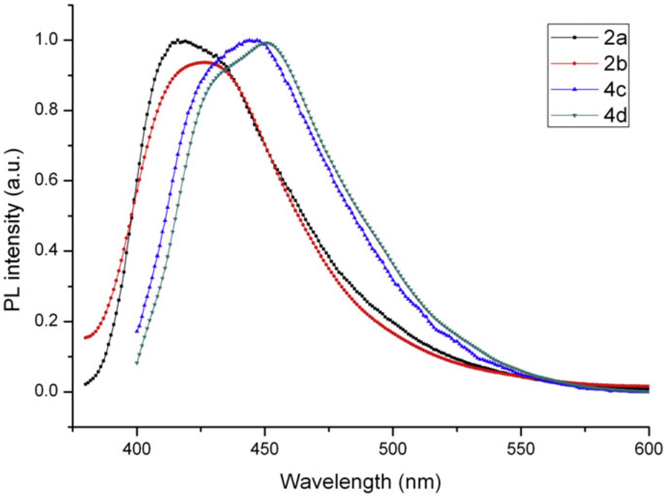


Fig. 7. PL spectra of compounds (**2a**, **2b**, **4c**, **4d**) in CH_2Cl_2 solution.

Meanwhile, we also studied the effects of the introduction of an aryl-acrylonitrile group. We compared the absorption bands and emission spectra of compounds **4c**, **4d** with (Z)-2-phenyl-3-(4-phenylthiophen-2-yl)acrylonitrile (**2b**) and (Z)-3-(4-(4-methoxyphenyl) thiophen-2-yl)-2-phenylacrylonitrile (**2d**) respectively, as shown in Fig. 7. The only difference between these compounds is the introduction of a biphenyl-acrylonitrile group. That the UV–vis bands and PL spectra of **4c**, **4d** in CH_2Cl_2. solution and in the solid state are all red shifted significantly. With the introduction of a phenyl-acrylonitrile group, the extended conjugated chain attributes to the red shift in these compounds.

4. Conclusions

In conclusion, several novel 4-aryl substituted thiophene derivatives with bis-diarylacrylonitrile unit have been efficiently synthesized. The absorption and photoluminescent spectra of these derivatives in CH_2Cl_2 and THF were investigated. These compounds exhibit similar absorption and emission behaviors and emit strongly in solution and solid state, with the emission maximal in the range of 400–500 nm.

Acknowledgments

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