Dyes and Pigments 88 (2011) 301–306

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis and photoluminescence characteristics of novel α,β-diarylacrylonitrile derivatives containing both a biphenyl group and a triphenylamine unit

Bao Li, Qian Li, Bin Liu, Youfeng Yue, Mingxin Yu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 19 April 2010
Received in revised form
27 July 2010
Accepted 27 July 2010
Available online 5 August 2010

Keywords:
Triphenylamine
Diarylacrylonitrile
Suzuki reaction
Photoluminescence
Biphenyl
OLEDs

ABSTRACT

2-(4-Bromophenyl)-3-(4-diphenylaminophenyl)acrylonitrile was prepared by the base catalysed condensation of 4-diphenylaminobenzaldehyde and 2-(4-bromophenyl)acetonitrile. A series of α,β-diarylacrylonitrile derivatives containing both a biphenyl group and a triphenylamine unit were synthesized from 2-(4-bromophenyl)-3-(4-diphenylaminophenyl)acrylonitrile and boronic acids via a Suzuki reaction. The structures of these compounds were characterized using FTIR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The UV–vis absorption and photoluminescent spectra of these derivatives were investigated. These compounds emit green fluorescence with maximum emission peaks of 500–550 nm in CH_2Cl_2 solution and in the solid state under UV irradiation. Analysis revealed good thermal stability with a decomposition temperature ranging from 279–386 °C.

1. Introduction

Considerable studies have been made on organic light emitting diodes (OLEDs) for their potential applications in next generation full-colour displays as a promising alternative to the conventional liquid crystal displays [1–4]. Among the various kinds of OLED materials, triarylamine derivatives have been widely investigated for almost two decades because these compounds have showed excellent thermal and electrochemical stability, electron-donating ability, optoelectronic properties [5–9] and they are standard hole transport materials [10–14].

Triphenylamine derivatives have been widely used as dyes [7,14] and α,β-diarylacrylonitriles attract interest since nitriles serve as versatile intermediates in the synthesis of variety of products such as perfumes, sex-pheromones, vitamin A, and pigments [15,16]. Furthermore, aromatic compounds based on biphenyls also play an important role in their applications in OLEDs as well as in dyes and pigments because of their easy synthesis and highly polarizable π-electron systems [17,18].

Based on our studies in the field of organic light emitting devices [5,19], as well as in palladium-catalysed coupling reactions [6,10,11], we became interested in the preparation of new functionalized triphenylamine derivatives. In the present article, we report the design and synthesis of a series of novel α,β-diarylacrylonitrile derivatives containing both a biphenyl group and a triphenylamine unit and which offer potential application as dyes, pigments and OLED materials [20–24]. The structure of the compounds was characterized using FTIR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The general properties such as solubility and thermal properties are reported. Their ultraviolet–visible spectrum (UV–vis) and photoluminescence (PL) properties were recorded.

2. Experimental

2.1. Materials

Palladium, boronic acids, Na_2CO_3, dimethoxyethane were purchased from Aldrich Chemical Co. Sodium tert-butoxide was purchased from Alfa-Aesar. Toluene was distilled under nitrogen from molten sodium. 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. ^{1}H and ^{13}C NMR spectra were run on a Bruker AV-400 NMR spectrometer in $CDCl_3$. IR

---

* Corresponding author. Tel.: +86 571 87979519; fax: +86 571 87951895.
E-mail address: mingxinyu@css.zju.edu.cn (M. Yu).

0143-7208/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2010.07.010

spectra were recorded in KBr on a Nicolet NEXUS 470 FTIR spectrophotometer. Vibrational transition frequencies were reported in wave numbers (cm^{-1}). Mass spectra were obtained on HP5989B mass spectrometer. Elemental analyses were determined using a Perkin–Elmer 240 analyzer. UV–vis spectra were recorded on a Hitachi U-3300 model while PL spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer. Thermo gravimetric analysis (TGA) was performed on Waters DSC Q100.

2.3. Synthesis

*2.3.1. General procedure for the synthesis of triphenylamines containing α,β-diarylacrylonitriles (**3a**–**e**)*

A solution of the aromatic aldehyde (1.0 mmol) and aromatic acetonitrile (1.0 mmol) in absolute EtOH (10 mL) was treated portion wise with NaOMe (0.1 mmol), stirred at room temperature for 1–2 h, cooled to 0 °C, and filtered. The precipitate was washed with cool EtOH.

*2.3.1.1. (Z)-2-(4-chlorophenyl)-3-(4-diphenylaminophenyl)acrylonitrile (**3a**).* Yellow solid. Yield: 82%. M.p. 147–148 °C. FTIR (KBr pellet, cm^{-1}): 3063, 3034, 2214, 1608, 1585, 1514, 1491, 1329, 1298, 1251, 1185, 1178, 829, 757, 706, 696. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.75 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.35–7.38 (m, 3H), 7.28–7.32 (m, 4H), 7.09–7.15 (m, 6H), 7.02 (d, J = 9.2 Hz, 2H). ^{13}C NMR (400 MHz, CDCl$_3$): δ_c: 155.5, 148.2, 136.4, 135.0, 134.3, 133.0, 129.8, 129.5, 129.2, 129.0, 128.4, 127.5, 127.4, 126.3, 119.3. MS *m*/*z*: 406 (M$^+$). Anal. Calcd for $C_{27}H_{19}ClN_2$: C, 79.70; H, 7.71; N, 6.88. Found: C, 79.66; H, 7.73; N, 6.85.

*2.3.1.2. (Z)-3-(4-diphenylaminophenyl)-2-phenylacrylonitrile (**3b**) [25].* Yellow solid. Yield: 89%. M.p. 145–146 °C. FTIR (KBr pellet, cm^{-1}): 3058, 3033, 2216, 1584, 1507, 1489, 1329, 1297, 1274, 1178, 759, 696. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.80 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.43–7.46 (m, 3H), 7.32–7.39 (m, 5H), 7.12–7.19 (m, 6H), 7.07 (d, J = 8.8 Hz, 2H). ^{13}C NMR (400 MHz, CDCl$_3$): δ_c: 148.0, 146.4, 141.8, 137.9, 130.7, 129.9, 129.7, 127.8, 127.6, 125.8, 122.9, 122.6, 122.4, 118.8, 108.5.

*2.3.1.3. (Z)-3-(4-diphenylaminophenyl)-2-p-tolylacrylonitrile (**3c**).* Yellow solid. Yield: 85%. M.p. 120–121 °C. FTIR (KBr pellet, cm^{-1}): 3052, 3035, 2214, 1585, 1512, 1504, 1488, 1328, 1296, 1192, 1178, 828, 815, 757, 695. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.79 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.41 (s, 1H), 7.32–7.36 (m, 4H), 7.24–7.27 (m, 2H), 7.13–7.20 (m, 6H), 7.07 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (400 MHz, CDCl$_3$): δ_c: 149.7, 146.7, 140.7, 138.7, 132.2, 130.5, 129.7, 129.5, 126.7, 125.6, 125.5, 124.3, 121.0, 118.8, 107.8, 21.2. MS *m*/*z*: 386 (M$^+$). Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.52. Found: C, 86.89; H, 5.83; N, 7.63.

*2.3.1.4. (Z)-3-(4-diphenylaminophenyl)-2-(4-methoxyphenyl)acrylonitrile (**3d**) [26].* Yellow solid. Yield: 90%. M.p. 118–120 °C. FTIR (KBr pellet, cm^{-1}): 3052, 3031, 2214, 1608, 1585, 1514, 1491, 1298, 1251, 1185, 1178, 1035, 829, 757, 696. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.80 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.35–7.39 (m, 5H), 7.15–7.22 (m, 6H), 7.11 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (400 MHz, CDCl$_3$): δ_c: 160.0, 149.6, 146.8, 139.8, 130.4, 129.6, 127.6, 127.0, 126.9, 125.6, 124.2, 121.2, 118.8, 114.4, 107.6, 55.4.

*2.3.1.5. (Z)-2-(4-bromophenyl)-3-(4-diphenylaminophenyl)acrylonitrile (**3e**).* Yellow solid. Yield: 85%. M.p. 143–144 °C. FTIR (KBr pellet, cm^{-1}): 3063, 3034, 2212, 1638, 1578, 1535, 1508, 1492, 1333, 1193, 1179, 1075, 751, 698. ^{1}HNMR (400 MHz, CDCl$_3$) δ_H: 7.76 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.39 (s, 1H), 7.32 (m, 4H), 7.10–7.17 (m, 6H), 7.03 (d, J = 8.8 Hz, 2H). ^{13}C NMR (400 MHz, CDCl$_3$): δ_c: 150.3, 146.5, 142.0, 134.1, 132.1, 130.7, 129.6, 127.1, 126.0, 125.8, 124.5, 122.6, 120.7, 118.4, 106.4. MS *m*/*z*: 465 (M$^+$). Anal. Calcd for $C_{28}H_{22}BrN_2$: C, 72.11; H, 4.75; N, 6.01. Found: C, 72.02; H, 4.83; N, 6.12.

*2.3.2. General procedure for the synthesis of α,β-diarylacrylonitrile derivatives containing both biphenyl group and triphenylamine (**4a**–**e**)*

A degassed mixture of 2-(4-bromophenyl)-3-(4-diphenylaminophenyl) acrylonitrile (1.0 mmol), Na_2CO_3 (2.2 mmol), water (1.1 mL), EtOH (0.8 mL), dimethoxyethane (2.5 mL), boronic acids (1.2 mmol), and $Pd(PPh_3)_4$ (0.01 mmol) was heated under reflux for an appropriate length of time. The reaction mixture was allowed to cool to room temperature, and the inorganic material was filtered off. The filtrate was concentrated under reduced pressure, and the resulting crude oil was chromatographed on silica gel to afford the target compounds **4a**–**e** (eluent: ethyl acetate and hexane).

*2.3.2.1. (Z)-2-biphenyl-4-yl-3-(4-diphenylaminophenyl)acrylonitrile (**4a**).* Yellow solid. Yield: 92%. M.p. 185 °C. FTIR (KBr pellet, cm^{-1}): 3029, 2210, 1582, 1506, 1488, 1450, 1428, 1333, 1298, 1273, 1194, 1179, 846, 834, 763, 757, 704, 696. ^{1}H NMR (400, CDCl$_3$) δ_H: 7.80 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.67–7.62(m, 4H), 7.47 (d, J = 4.0 Hz), 7.45(s, 1H), 7.40–7.31(m, 5H), 7.18–7.11(m, 6H), 7.07–7.05(d, J = 8.4 Hz, 2H). ^{13}C NMR (400 MHz, CDCl$_3$) δ_c: 150.0(C), 146.6(CH), 141.3(C), 141.3(C), 140.1(C), 133.9(C), 130.7(CH), 129.6 (CH), 128.9(CH), 127.7(C), 127.6(CH), 127.0(CH), 126.4(C), 126.1(CH), 125.7(CH), 124.4(CH), 120.1(CH), 118.8(C), 107, 2(C). MS *m*/*z*: 448 (M$^+$). Anal. Calcd for $C_{33}H_{24}N_2$: C, 88.36; H, 5.39; N, 6.25. Found: C, 88.33; H, 5.37; N, 6.30.

*2.3.2.2. (Z)-3-(4-diphenylaminophenyl)-2-(4′-methylbiphenyl-4-yl) acrylonitrile (**4b**).* Yellow solid. Yield: 94%. M.p. 192–194 °C. FTIR (KBr pellet, cm^{-1}): 3033, 2923, 2211, 1583, 1507, 1489, 1332, 1297, 1270, 1194, 1180, 1074, 1008, 810, 759, 700, 532. ^{1}H NMR (400, CDCl$_3$) δ_H: 7.79(d, J = 8.0 Hz, 2H), 7.70(d, J = 8.0 Hz, 2H), 7.63(d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.46(s, 1H), 7.33–7.25(m, 6H), 7.17–7.10(m, 6H), 7.06(d, J = 8.4 Hz, 2H), 2.40(s, 3H). ^{13}C NMR (400 MHz, CDCl$_3$) δ_c: 149.9(C), 146.6(CH), 141.3(C), 141.2(C), 137.6 (C), 133.6(C), 130.7(CH), 129.6(CH), 129.6(CH), 127.4(CH), 126.8(CH), 126.5(C), 126.0(CH), 125.7(CH), 124.3(CH), 120.9(CH), 118.8(C), 107.3 (C), 21.1(CH$_3$). MS *m*/*z*: 462 (M$^+$). Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.23; H, 5.73; N, 6.04.

*2.3.2.3. (Z)-3-(4-diphenylaminophenyl)-2-(4′-methoxybiphenyl-4-yl)acrylonitrile (**4c**).* Yellow solid. Yield: 96%. M.p. 171–173 °C. FTIR (KBr pellet, cm^{-1}): 3034, 2957, 2835, 2212, 1583, 1506, 1493, 1333, 1286, 1273, 1194, 1180, 1040, 1027, 818, 732, 700, 531. ^{1}H NMR (400, CDCl$_3$) δ_H: 7.78(d, J = 8.4 Hz, 2H), 7.68(d, J = 8.4 Hz, 2H), 7.60(d, J = 8.0 Hz, 2H), 7.55(d, J = 8.4 Hz, 2H), 7.45(s, 1H), 7.31(dd, J = 8.0 Hz, J = 7.6 Hz, 4H), 7.17-7.10(m, 6H), 7.05(d, J = 8.8 Hz, 2H), 6.99(d, J = 8.4 Hz, 2H), 3.85(s, 3H). ^{13}C NMR (400 MHz, CDCl$_3$) δ_c: 159.5(C), 149.9(C), 146.6(CH), 141.0(C), 140.9(C), 133.3(C), 132.5(C), 130.6(CH), 129.6(CH), 128.0(CH), 127.1(CH), 126.5(C), 126.0(CH), 125.7(CH), 124.4(CH), 120.9(CH), 118.8(C), 114.3(CH), 107.3(C), 55.4(CH$_3$). MS *m*/*z*: 478 (M$^+$). Anal. Calcd for $C_{34}H_{26}N_2O$: C, 85.33; H, 5.48; N, 5.85. Found: C, 85.38; H, 5.54; N, 5.74.

*2.3.2.4. (Z)-2-(3′,5′-dimethylbiphenyl-4-yl)-3-(4-diphenylaminophenyl)acrylonitrile (**4d**).* Yellow solid. Yield: 75%. M.p. 75 °C. FTIR (KBr pellet, cm^{-1}): 3027, 2913, 2348, 2204, 1584, 1506, 1492, 1380, 1332, 1285, 1193, 1179, 836, 755, 697. ^{1}H NMR (400, CDCl$_3$) δ_H: 7.83(d, J = 8.4 Hz, 2H), 7.73(d, J = 8.4 Hz, 2H), 7.48(s, 1H), 7.35(dd, J = 6.8 Hz, J = 8.0 Hz, 4H), 7.27 (s, 2H), 7.21–7.16(m, 6H), 7.10(d, J = 7.6 Hz, 2H), 7.06(s, 1H), 2.43(s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_C: 149.9(C), 146.7 (CH), 141.6(C), 141.2(C), 140.1(C), 138.5(CH), 133.7(C), 130.7(CH), 129.7 (CH), 129.4(C), 127.6(CH), 126.5(C), 126.0(CH), 125.8(CH), 125.0(CH), 124.4(CH), 120.9(CH), 118.9(C), 107.4(C), 21.5(CH_3). MS *m*/*z*: 476 (M^+). Anal. Calcd for $C_{35}H_{28}N_2$: C, 88.20; H, 5.92; N, 5.88. Found: C, 88.15; H, 5.91; N, 5.94.

*2.3.2.5. (Z)-3-(4-diphenylaminophenyl)-2-(4-(naphthalen-2-yl) phenyl)acrylonitrile (**4e**).* Yellow solid. Yield: 78%. M.p. 199–200 °C. FTIR (KBr pellet, cm^{-1}): 3057, 2352, 2209, 15814, 1507, 1490, 1334, 1274, 1193, 1179, 815, 756, 700. ^{1}H NMR (400, $CDCl_3$) δ_H: 8.09(s, 1H), 7.95(d, $J = 8.8$ Hz, 1H), 7.93(d, $J = 7.6$ Hz, 1H), 7.89(d, $J = 8.0$ Hz, 1H), 7.84–7.77(m, 7H), 7.52(d, $J = 6.8$ Hz, 3H), 7.34(dd, $J = 8.0$ Hz, $J = 7.6$ Hz, 4H), 7.20–7.13(m, 6H), 7.08(d, $J = 8.8$ Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_C: 150.0(C), 146.6(CH), 141.4(C), 141.2(C), 137.4 (C), 134.0(C), 133.6(C), 132.8(C), 130.7(CH), 129.6(CH), 128.6(CH), 128.2(CH), 127.8(CH), 127.7(CH), 126.5(C), 126.4(CH), 126.2(CH), 126.1(CH), 125.8(CH), 125.7(CH), 125.2(CH), 124.4(CH), 120.9(CH), 118.8(C), 107.2(C). MS *m*/*z*: 498 (M^+). Anal. Calcd for $C_{37}H_{26}N_2$: C, 89.13; H, 5.26; N, 5.62. Found: C, 89.03; H, 5.41; N, 5.56.

3. Results and discussion

3.1. Synthesis

The target compounds **4a**–**e** were prepared via a four-step procedure which is shown in Scheme 1.

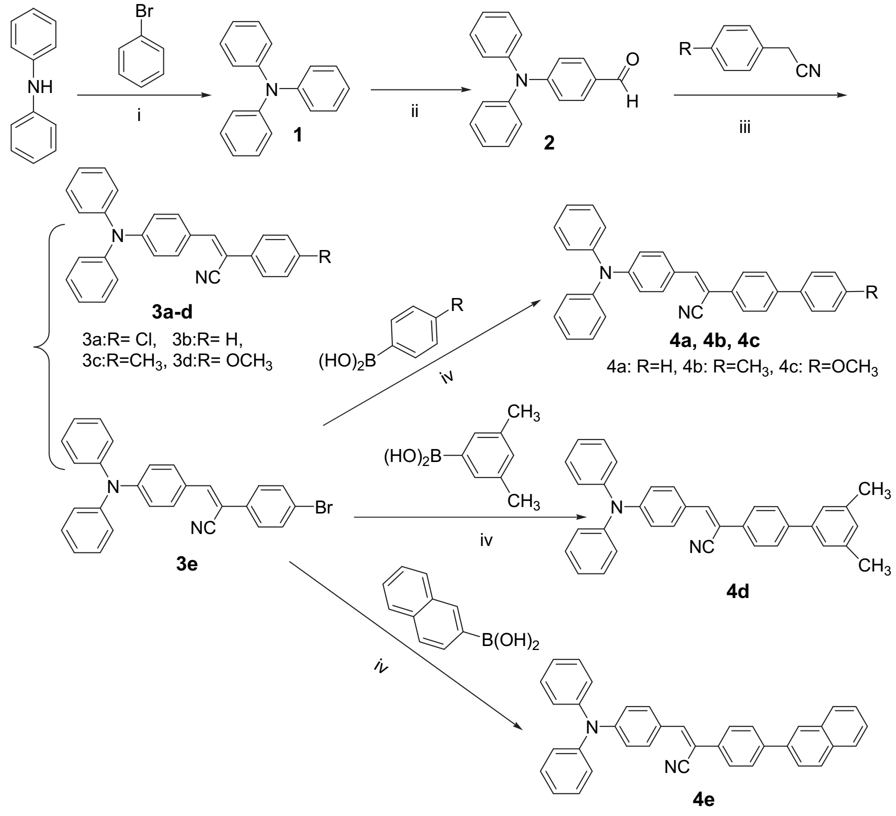
Compound **1** was prepared from diphenylamine and 1-bromobenzene according to well-known chemistry [27,28]. Compound **2** was synthesized according to a literature procedure [12]. α,β–diarylacrylonitrile derivatives **3a**–**e** were prepared by the base catalysed condensation between compound **2** and an aromatic acetonitrile. In the last step of the sequence compound **3e** was coupled with various boronic acids to afford a series of α,β-diarylacrylonitrile derivatives containing both a biphenyl group and a triphenylamine unit by the Suzuki reaction.

Palladium-catalysed cross coupling reaction is widely used in the construction of aryl C–C bond [29–32]. Suzuki coupling of aryl halides and aryl boronic acids is a powerful method for the synthesis of biaryl compounds [33–36]. In this work, we used the catalytic system of $Pd(PPh_3)_4$ to prepare compounds (**4a**–**e**), Na_2CO_3 was used as the base and the solvent system employed was a mixture of DME, EtOH and H_2O. The ligand-free catalyst was particularly efficient in this system and the yields were consistently in the 78–96% range. The reaction times and yields are shown in Table 1.

The thermal properties of **3a**–**e** and **4a**–**e** were investigated by TGA. Decomposition temperature curves are shown in Fig. 1. The TGA data (Table 1) show thermal stability up to 279–386 °C. Series 4 have higher decomposition temperature than series **3**, the results indicate that the incorporation of a biphenyl group into series 3 enhances the thermal properties significantly.

3.2. Photophysical properties

Most light emitting electrofluorescent molecules were designed based on the electron-donating and electron-withdrawing groups on a conjugated system. Here a nitrile function is employed as an electron



Conditions: (i) $Pd(OAc)_2$, P(*o*-tolyl)$_3$, NaO-*t*-Bu, Toluene, 110°C; (ii) DMF, $POCl_3$; (iii) $NaOCH_3$, Ethanol, rt, (iv) $Pd(PPh_3)_4$, Na_2CO_3, DME, Ethanol: H_2O(1:1.25).

Scheme 1. Synthesis of α,β-diarylacrylonitrile derivatives (**3a**–**e**) and (4**a**–**e**).

Table 1
Reaction times, yields and thermal properties of compounds (**3a**–**e**) and (**4a**–**e**).

Entry	Reaction time [h]	Yield [%]	T_m[a] [°C]	T_d[b] [°C]
3a	1.5	82	148	279
3b	1	85	145	285
3c	1	89	121	284
3d	2	85	118	288
3e	2	90	144	283
4a	4	92	185	356
4b	4	94	193	333
4c	4	96	172	386
4d	8	85	75	311
4e	10	78	199	341

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

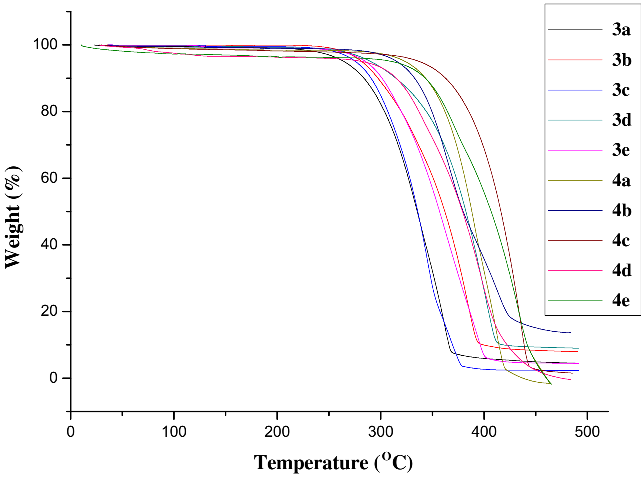


Fig. 1. TGA spectra of compounds (**3a**–**e**) and (**4a**–**e**).

withdrawing group and the triphenylamine group is the election donor function. In order to investigate the photophysical properties of these groups, the UV–vis absorption and PL spectra of compounds (**3a**–**e**, **4a**–**e**) in different solutions were recorded. The spectral data are summarized in Table 2, and the UV–vis and PL spectra of these compounds in CH_2Cl_2 solution are shown in Figs. 2 and 3.

In the UV–vis absorption spectra between 280 and 450 nm, two bands were clearly observed for these derivatives and the behavior are quite similar to each other. They reveal a common low-energy broad band at 350–450 nm assigned to the π–π^* transitions of the compounds. The absorption bands at 280–350 nm come from the combination of the n–π^* transition of triphenylamine moieties. The absorption bands of each compound in cyclohexane and toluene were also recorded in Table 2. These absorption bands are relatively insensitive to the solvents compared with the corresponding emission bands. Variations of less than 7 nm were observed in different polar solvents.

For the emission spectra in CH_2Cl_2 solution, as shown in Fig. 3, all of the compounds display similar behavior and yield green

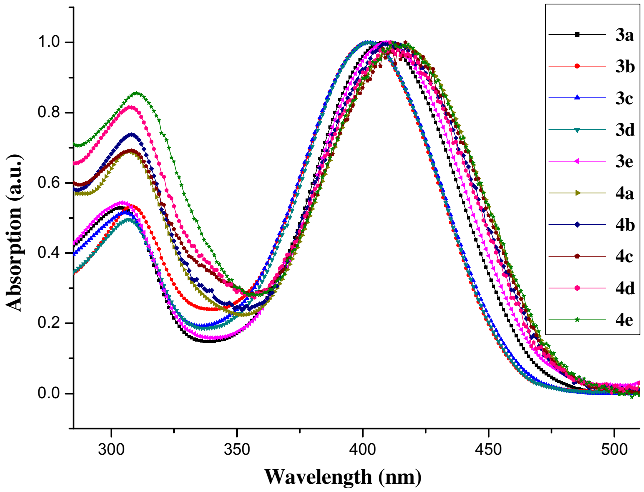


Fig. 2. Absorption spectra of compounds (**3a**–**e**) and (**4a**–**e**) in CH_2Cl_2 solution.

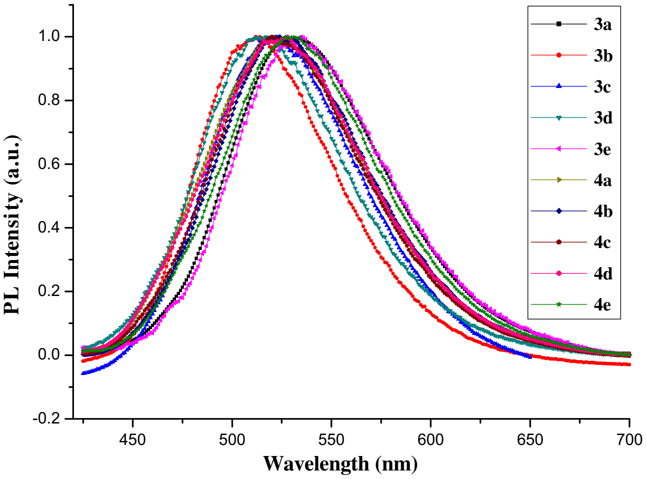


Fig. 3. PL spectra of compounds (**3a**–**e**) and (**4a**–**e**) in CH_2Cl_2 solution.

Table 2
Photophysical properties of compounds (**3a**–**e**) and (4**a**–**e**).

Entry	CH_2Cl_2 λ_{abs} [nm]	CH_2Cl_2 λ_{em} [nm]	Toluene λ_{abs} [nm]	Toluene λ_{em} [nm]	Cyclohexane λ_{abs} [nm]	Cyclohexane λ_{em} [nm]	Solid λ_{em} [nm]	ε[a] [mol L^{-1} cm^{-1}]	Φ_f[b] [%]
3a	305, 409	535	306, 408	483	305, 405	466	512	14172, 25208	8.2
3b	306, 403	524	307, 402	471	306, 397	445	504	14568, 28128	9.8
3c	307, 402	513	308, 401	473	307, 397	448	505	16126, 30146	7.6
3d	308, 402	512	309, 402	470	308, 397	446	503	19108, 34944	14.2
3e	304, 409	529	306, 409	479	305, 406	461	523	22407, 39159	8.5
4a	308, 416	522	309, 419	487	307, 412	457	511	22837, 31561	27.2
4b	308, 411	524	309, 417	486	307, 410	457	525	23402, 29924	12.6
4c	308, 414	520	308, 410	485	307, 407	457	545	26858, 32982	18.7
4d	308, 413	526	308, 412	484	307, 406	457	530	18469, 23634	11.2
4e	310, 412	525	310, 409	487	308, 406	463	547	27258, 30981	12.4

[a] Extinction coefficients determined in CH_2Cl_2 solutions when the concentration of each compound is 1.0×10^{-5} M.
[b] Relative quantum yields (with fluorescein in THF $\Phi_f = 0.93$ as a standard).

emission at room temperature. The maximal emission peaks are mainly located at about 510–540 nm. The emission spectra of these compounds in cyclohexane and toluene were also recorded in Table 2. It can be seen that the emission spectra of compounds **3a**–**e** and **4a**–**e** show significant difference in different solvents, the average maximal emission peak is about 520 nm in CH_2Cl_2 solution, while in cyclohexane and toluene solution, they are 460 nm and 480 nm respectively. A change of the solvent from cyclohexane to toluene resulted in about 20 nm red shift of the emission maximum, similarly, when the solvent changed from toluene to CH_2Cl_2, about a 40 nm red shift of the emission maximum of these compounds occurred. The polarity of the solvent plays an important role on the photophysical properties in such strong donor–acceptor systems.

Emission spectra of compounds **3a**–**e** and **4a**–**e** in the solid state were determined with an excitation wavelength of 400 nm, the results are shown in Table 2 and Fig. 4. These compounds have relatively small stokes shifts in the range 100–150 nm. The emission peaks of compounds **4a**–**e** in the solid state show a small red shift compared to **3b** which is attributed to the introduction of biphenyl groups.

Extinction coefficients of UV–vis absorption maximum were calculated and recorded in Table 2, compounds **3a**–**e** and **4a**–**e** have extinction coefficients range of 1.4×10^4–2.7×10^4 mol L^{-1} cm^{-1} at 300 nm and 2.3×10^4–3.9×10^4 mol L^{-1} cm^{-1} at 400 nm in CH_2Cl_2 solution. The fluorescence quantum efficiencies of compounds **3a**–**e** and **4a**–**e** were determined in tetrahydrofuran (Table 2). Their Φ_f is between 7.6 and 27.2%.

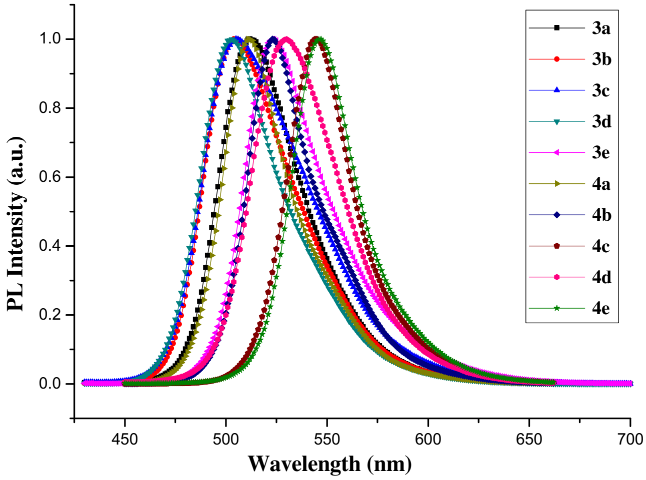


Fig. 4. PL spectra of compounds (**3a**–**e**) and (**4a**–**e**) in the solid state.

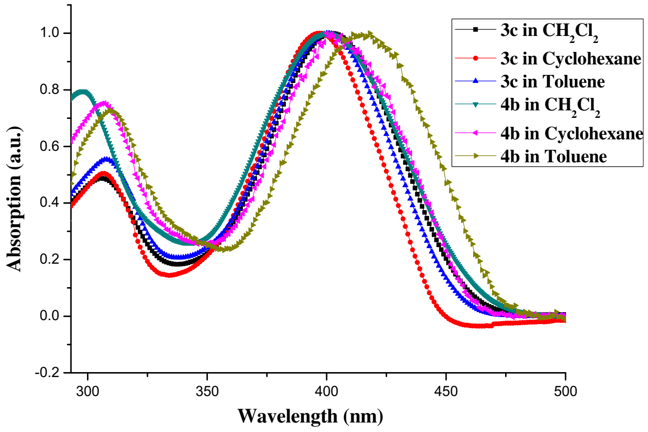


Fig. 5. Absorption spectra of compounds **3c** and **4b** in different solutions.

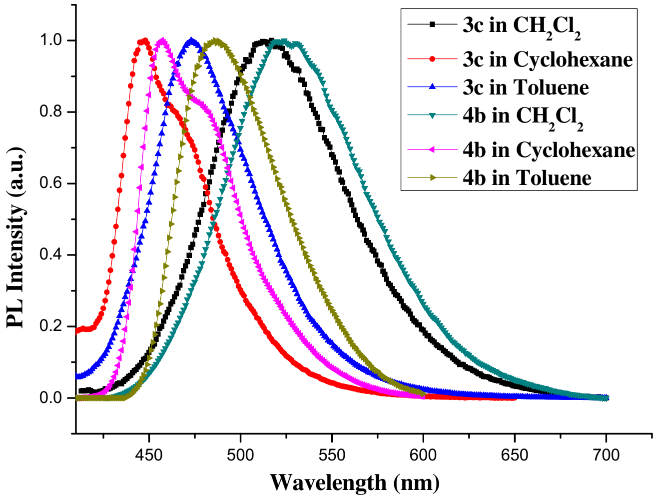


Fig. 6. PL spectra of compounds **3c** and **4b** in different solutions.

The introduction of a biphenyl group into series **3** resulted in the change of their photophysical properties (Table 2). In order to study the effects on photophysical properties after introducing the biphenyl group, comparisons between series **3** and series **4** were made. Figs. 5 and 6 exibit the absorption bands and emission spectra of compounds **3c** and **4b** in different solvents. Compounds **3c** and **4b** have the same R group ($-CH_3$), the only difference is that **4b** has a biphenyl group thus it has a longer conjugation pathway. It can be found that the UV–vis bands and PL spectra of **4b** in different solvents and in the solid state are all red shifted relative to those of **3c**. Furthermore, quantum yields are also improved when the conjugation of the system increased. Similar results can also be found between **3b** and **4a**, and **3d** and **4c** when the R groups are H, and OMe, respectively.

4. Conclusions

In conclusion, several novel α,β-diarylacrylonitrile derivatives containing both a biphenyl group and a triphenylamine unit have been efficiently synthesised. The absorption and photoluminescent spectra of these derivatives in different solutions were investigated. These compounds exhibit similar absorption and emission behavior and emit strongly in solution and in the solid state, with the emission maxima in the range of 500–550 nm. The compounds exhibit good thermal stability with a decomposition temperature range from 279–386 °C.

Acknowledgements

The project is sponsored by the Natural Science Foundation for the Education Ministry of Zhejiang Province.

References

[1] Tang CW, Slyke Van. Organic electroluminescent diodes. Applied Physics Letters 1987;51:913–5.
[2] Lin HQ, Chen BJ, Zhang XH, Lee CS, Kwong HL, Lee ST. A novel yellow fluorescent dopant for high-performance organic electroluminescent devices. Chemistry of Materials 2001;13:456–8.
[3] Namai H, Ikeda H, Hoshi Y, Kato N, Morishita Y, Mizuno K. Thermoluminescence and a new organic light-emitting diode (OLED) based on triplet-triplet fluorescence of the trimethylenemethane (TMM) biradical. Journal of the American Chemical Society 2007;129:9032–6.
[4] Froehlich JD, Young R, Nakamura T, Ohmori Y, Li S, Mizochuki A. Synthesis of multi-functional POSS emitters for OLED applications. Chemistry of Materials 2007;19:4991–7.

[5] Yu MX, Chang LC, Lin CH, Duan JP, Wu FI, Chen IC, et al. Luminescence properties of aminobenzanthrones and their application as host emitters in organic light-emitting devices. Advanced Functional Materials 2007;17: 369–78.

[6] Yue YF, Kang JH, Yu MX. The synthesis and photophysical properties of novel triphenylamine derivatives containing α, β-diarylacrylonitrile. Dyes and Pigments 2009;83:72–80.

[7] Ning ZJ, Zhang Q, Wu WJ, Pei HC, Liu B, Tian H. Starburst triarylamine based dyes for efficient dye-sensitized solar cells. The Journal of Organic Chemistry 2008;73(10):3791–7.

[8] Hua JL, Li B, Meng FS, Ding F, Qian SX, Tian H. Two-photon absorption properties of hyperbranched conjugated polymers with triphenylamine as the core. Polymer 2004;45(21):7143–9.

[9] Meng FS, Mi J, Qian SX, Chen KC, Tian H. Linear and tri-branched copolymers for two-photon absorption and two-photon fluorescent materials. Polymer 2003;44:6851–5.

[10] Yu MX, Chen XH, Cheng CH. Study on synthesis of organic light emitting diode materials of aminoanthrancenes and their light emitting property. Chinese Journal of Organic Chemistry 2005;25:218–21.

[11] Yu MX, Wang MJ, Chen XH, Hong BB, Zhang XY, Cheng CH. Synthesis of OLED materials of several triarylamines by palladium catalysts and their light emitting property. Journal of Chemical Research 2005;9:558–60.

[12] Sengupta S, Sadhukhan SK, Muhuri S. A tetraphenylmethane based starburst triarylamine cluster:spectroscopy, electrochemistry and morphological studies. Tetrahedron Letters 2002;43:3521–4.

[13] Zhao HD, Tanjutco C, Thayumanavan S. Design and synthesis of stable triarylamines for hole-transport applications. Tetrahedron Letters 2001;42:4421–4.

[14] Tian HN, Yang XC, Chen RK, Zhang R, Hagfeldt A, Sun LC. Effect of different dye baths and dye-structures on the performance of dye-sensitized solar cells based on triphenylamine dyes. The Journal of Physical Chemistry C 2008;112 (29):11023–33.

[15] Fringuelli F, Pani G, Piermatti O, Pizzo F. Condensation reactions in water of active methylene compounds with arylaldehydes: one-pot synthesis of flavonols. Tetrahedron 1994;50:11499–508.

[16] D'Sa BA, Kisanga P, Verkade JG. Direct synthesis of alpha, beta- unsaturated nitriles catalyzed by nonionic superbases. The Journal of Organic Chemistry 1998;63:3961–7.

[17] Lye J, Freeman HS, Cox RD. Molecular modeling of Congo Red analogues containing terphenyl and quarterphenyl moieties. Dyes and Pigments 2000;47:53–64.

[18] Dinçer HA, Gonca E, Gűl A. The synthesis and spectral properties of novel phthalocyanines with pendant bulky units. Dyes and Pigments 2008;79:166–9.

[19] Yu MX, Duan JP, Lin CH, Cheng CH, Tao YT. Diaminoanthracene derivatives as high-performance green host electroluminescent materials. Chemistry of Materials 2002;14:3958–63.

[20] Zhou Y, He QG, Yang Y, Zhong HZ, He C, Sang GY, et al. Binaphthyl-containing green- and red-emitting molecules for solution-processable organic light-emitting diodes. Advanced Functional Materials 2008;18:3299–306.

[21] Li ZH, Wong MS, Tao Y, D'Iorio M. Synthesis and functional properties of strongly luminescent diphenylamino end-capped oligophenylenes. The Journal of Organic Chemistry 2004;69:921–7.

[22] Vezzu DAK, Deaton JC, Shayeghi M, Li YM, Huo SQ. Acridinone/amine(carbazole)-based bipolar molecules: efficient hosts for fluorescent and phosphorescent emitters. Organic Letters 2009;11:4310–3.

[23] Ge ZY, Hayakawa T, Ando S, Ueda M, Akiike T, Miyamoto H, et al. Spin-coated highly efficient phosphorescent organic light-emitting diodes based on bipolar triphenylamine-benzimidazole derivatives. Advanced Functional Materials 2008;18:584–90.

[24] Ko CW, Tao YT. Organic light-emitting diodes based on 2-(stilben-4-yl) benzoxazole derivatives: an implication on the emission mechanism. Chemistry of Materials 2001;13:2441–6.

[25] Hisahiro H, Kazumasa W, Akira K. Electrophotographic photoreceptors. JP 61259256(A), 1986–11–17.

[26] Masabumi O, Teruyuki O, Fumio K, Hirota S, Toshihiko T. Electroluminescent devices. JP 03205477(A), 1991–9–6.

[27] Wolfe JP, Tomori H, Sadighi JP, Yin J, Buchwald SL. Simple, efficient catalyst system for the palladium-catalyzed amination of aryl chlorides, bromides, and triflates. The Journal of Organic Chemistry 2000;65:1158–74.

[28] Goodson FE, Hauck SI, Hartwig JF. Palladium-catalyzed synthesis of pure, regiodefined polymeric triarylamines. Journal of the American Chemical Society 1999;121(33):7527–39.

[29] Hassan J, Svignon M, Gozzi C, Schulz E, Lemaire M. Aryl–aryl bond formation one century after the discovery of the Ullmann reaction. Chemical Review 2002;102:1359–469.

[30] Han J, Liu Y, Guo R. Facile synthesis of highly stable gold nanoparticles and their unexpected excellent catalytic activity for Suzuki-Miyaura cross-coupling reaction in water. Journal of the American Chemical Society 2009;131:2060–1.

[31] Cho JK, Najman R, Dean TW, Ichihara O, Muller C, Bradley M. Captured and cross-linked palladium nanoparticles. Journal of the American Chemical Society 2006;128:6276–7.

[32] Navarro O, Kelly III RA, Nolan SP. A general method for the Suzuki-Miyaura cross-coupling of sterically hindered aryl chlorides: synthesis of di-and tri-ortho-substituted biaryls in 2-propanol at room temperature. Journal of the American Chemical Society 2003;125:16194–5.

[33] Suzuki A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. Journal of Organometallic Chemistry 1999;576:147–68.

[34] Brath H, Mesková M, Putala M. Suzuki cross-coupling at the chiral groove of 1,1′-binaphthyl:Stereoconservation versus deracemization pathway. European Journal of Organic Chemistry; 2009:3315–8.

[35] Yin JJ, Buchwald SL. A catalytic asymmetric Suzuki coupling for the synthesis of axially chiral biaryl compounds. Journal of the American Chemical Society 2000;122:12051–2.

[36] Yu MX, Fang HY, Yue YF, Chen YC, Chen SW. Synthesis of a novel ligand containing phenyl pyridine. Synthetic Communications 2010;40:58–63.