Dyes and Pigments 83 (2009) 72–80

Contents lists available at ScienceDirect

Dyes and Pigments

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

The synthesis and photophysical properties of novel triphenylamine derivatives containing α, β-diarylacrylonitrile

Youfeng Yue, Junhui Kang, Mingxin Yu*

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, China

ARTICLE INFO

Article history:
Received 4 January 2009
Received in revised form
20 March 2009
Accepted 20 March 2009
Available online 5 April 2009

Keywords:
Triphenylamine
Aryl halides
Diarylamines
Pd-catalyzed
C–N bond formation
OLEDs

ABSTRACT

α, β-Diarylacrylonitrile halides were prepared by condensation of appropriate arylaldehydes and arylacetonitrile halides using a catalytic amount of $NaOCH_3$ at room temperature. The diarylamines were reacted with various α, β-diarylacrylonitrile halides to afford several triphenylamine compounds, which displayed efficient hole transportation in the presence of $Pd(OAc)_2/P(o\text{-tolyl})_3$ catalyst, thereby constituting organic light emitting device materials. The novel triphenylamine derivatives were characterized using FTIR, ^1H NMR, ^{13}C NMR, MS and elemental analysis. The UV–vis absorption and photoluminescence spectra of the compounds were investigated. The lowest absorption band of α, β-diarylacrylonitrile-containing, triphenylamine derivatives, which occurred at ~400 nm, was assigned to charge-transfer transitions with an emission at 500–574 nm in different solutions and in the solid state.

1. Introduction

Over the past years, organic light emitting diodes (OLEDs) [1–4] have attracted much attention owing to their application potential in flat-panel displays and solid-state lights. It is well known that triphenylamines have been widely used as dyes [5–7] as well as crucial components in OLEDs materials due to their excellent solubility, high thermal stability [8,9] and excellent electron donating ability [10] as well as high luminescence and hole-transporting efficiency [11,12]. Additionally, α, β-diarylacrylonitriles enjoy considerable economic interest since nitriles serve as versatile intermediates in the synthesis of various products such as perfumes, pheromones, vitamin A and pigments [13,14].

As a continuation of the author's long-standing interest in organic light emitting devices [15,16] and palladium-catalyzed coupling reactions [17,18], interest became focused on the preparation of novel, functionalised, triphenylamine derivatives as potential standard hole transport materials [19,20]. This paper reports the design and synthesis of several novel, triphenylamine derivatives with α, β-diarylacrylonitrile [21,22] that contain both a nitrile group and triphenylamine and which offer potential application as dyes, pigments and OLED materials. The structure of the compounds was characterized using FTIR, ^1H NMR, ^{13}C NMR, mass-spectral data and elemental analysis. Their ultraviolet–visible spectrum (UV) and photo-luminescence (PL) properties were recorded. During our investigation of luminescent organic compounds, we have observed that these triphenylamine derivatives with α, β-diarylacrylonitrile are efficient green emitters in solutions and in solid state when irradiated by UV light, with the emission maxima in the range of 500–574 nm resulting from charge-transfer transitions from the aryl amino group to the nitrile moiety.

2. Experimental

2.1. Materials

α, β-Diarylacrylonitrile halides **1a**–**1g** were synthesized according to the method previously reported [23]. Triphenylamines derivatives containing α, β-diarylacrylonitrile **2a**–**2n** were synthesized via C–N bond formation. Diarylamines, Palladium(II) and tri-o-tolylphosphine were purchased from Aldrich Chemical Co. Sodium *tert*-butoxide was purchased from Alfa-Aesar and stored in a vacuum atmospheres glove box under nitrogen. 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. Thermo gravimetric analysis

* 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 © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.03.014

(TGA) was performed on Mettler Toledo TGA/SDTA 851e. ^{1}H and ^{13}C NMR spectra were run on a Bruker AV-400 NMR spectrometer in $CDCl_3$. IR 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 Varian 500-MS. Element analysis was taken with 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.

2.3. Synthesis

2.3.1. General procedure for the synthesis of α, β-diarylacrylonitrile halides (**1a**–**1g**)

A solution of the aromatic aldehydes (1.0 mmol) and aromatic acetonitrile halides (1.0 mmol) in absolute EtOH (10 ml) was treated with NaOMe (0.1 mmol) portion wise, stirred at room temperature for 2–3 h, cooled to 0 °C, and filtered. The precipitate was washed with EtOH.

*2.3.1.1. (Z)-2-(4-bromophenyl)-3-phenylacrylonitrile (**1a**).* White solid. Yield: 92%. M.p. 135–137 °C. FTIR(KBr pellet, cm^{-1}): 3057, 2218, 1597, 1492, 822, 752. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (d, J = 8 Hz, 2H), 7.61–7.55 (m, 5H), 7.52–7.49(m, 3H). MS m/z: 284 (M + 1). Anal. Calcd for $C_{15}H_{10}BrN$: C, 63.40; H, 3.55; N, 4.93. Found: C, 63.43; H, 3.59; N, 4.91.

*2.3.1.2. (Z)-2-(4-bromophenyl)-3-p-tolylacrylonitrile (**1b**).* White solid. Yield: 95%. M.p. 120–122 °C. FTIR (KBr pellet, cm^{-1}): 3047, 2914, 2221, 1600, 1510, 1488, 825. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.82 (d, J = 8 Hz, 2H), 7.60–7.51 (m, 4H), 7.51 (s, 1H), 7.30 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H). MS m/z: 398 (M + 1). Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.43; H, 4.07; N, 4.72.

*2.3.1.3. (Z)-2-(4-bromophenyl)-3-(naphthalen-1-yl)acrylonitrile (**1c**).* Pale yellow solid. Yield: 93%. M.p. 179–180 °C. FTIR (KBr pellet, cm^{-1}): 3042, 2214, 1594, 1507, 1486, 986, 824, 774. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.29 (s, 1H), 8.09 (d, J = 7.2 Hz, 1H), 7.98–7.92 (m, 3H), 7.67–7.57 (m, 7H). MS m/z: 334 (M + 1). Anal. Calcd for $C_{19}H_{12}BrN$: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.31; H, 3.61; N, 4.18.

*2.3.1.4. (Z)-2-(4-bromophenyl)-3-(naphthalen-2-yl)acrylonitrile (**1d**).* White solid. Yield: 95%. M.p. 169–170 °C. FTIR (KBr pellet, cm^{-1}): 3051, 2214, 1606, 1581, 1561, 1490, 1078, 824, 745. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.29 (s, 1H), 8.09 (d, J = 8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H) 7.87 (d, J = 7.2 Hz, 1H), 7.67 (s, 1H), 7.60–7.53 (m, 6H). MS m/z: 334 (M + 1). Anal. Calcd for $C_{19}H_{12}NBr$: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.32; H, 3.59; N, 4.13.

*2.3.1.5. (Z)-3-(anthracen-9-yl)-2-(4-bromophenyl)acrylonitrile (**1e**).* Yellow solid. Yield: 89%. M.p. 210–212 °C. FTIR (KBr pellet, cm^{-1}): 3046, 3026, 2221, 1618, 1585, 1487, 880, 846, 825, 791, 735, 723. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.55 (s, 1H), 8.45 (s, 1H), 8.08 (d, J = 8 Hz, 2H), 8.02 (d, J = 8 Hz, 2H), 7.76 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.58–7.51 (m, 4H). MS m/z: 384 (M + 1). Anal. Calcd for $C_{23}H_{14}NBr$: C, 71.89; H, 3.67; N, 3.65. Found: C, 71.88; H, 3.62; N, 3.63.

*2.3.1.6. (Z)-2-(4-chlorophenyl)-3-p-tolylacrylonitrile (**1f**).* White solid. Yield: 95%. M.p. 106–108 °C. FTIR (KBr pellet, cm^{-1}): 3047, 2914, 2221, 1600, 1510, 1488, 825. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.79 (d, J = 8.0 Hz, 2H), 7.61–7.59 (m, 2H), 7.48 (s, 1H), 7.42–7.40 (m, 2H), 7.29–7.26 (m, 2H), 2.42 (s, 3H). MS m/z: 254 (M + 1). Anal. Calcd for $C_{16}H_{12}ClN$: C, 75.74; H, 4.77; N, 5.52. Found: C, 75.72; H, 4.75; N, 5.52.

*2.3.1.7. (Z)-2-(4-chlorophenyl)-3-(naphthalen-1-yl)acrylonitrile (**1g**).* Pale yellow solid. Yield: 92%. M.p. 174–175 °C. FTIR (KBr pellet, cm^{-1}): 3047, 2218, 1596, 1510, 1494, 1098, 829, 779, 765. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (s, 1H), 8.09 (d, J = 6.4 Hz, 1H), 7.98–7.92 (m, 3H), 7.72–7.70 (m, 2H), 7.61–7.57 (m, 3H), 7.49–7.46 (m, 2H). MS m/z: 290 (M + 1). Anal. Calcd for $C_{19}H_{12}ClN$: C, 78.76; H, 4.17; N, 4.83. Found: C, 78.78; H, 4.15; N, 4.80.

2.3.2. General procedure for the synthesis of triphenylamine derivatives with α, β-diarylacrylonitrile (**2a**–**2n**)

To a 25 ml sidearm flask was added α, β-diarylacrylonitrile halides (1.20 mmol), diarylamines (1.00 mmol), $Pd(OAC)_2$ (0.06 mmol, Pd/Br = 5%), P(*o*-tolyl)$_3$(0.18 mmol), and sodium *tert*-butoxide (1.50 mmol). To the flask was injected via a syringe toluene (10 ml). The reaction mixture was heated and stirred at 110 °C under nitrogen for an appropriate time until the reaction was complete. 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 acetic ether/hexane as eluents.

*2.3.2.1. (Z)-2-(4-(diphenylamino)phenyl)-3-phenylacrylonitrile (**2a**).* Pale yellow solid. Yield: 85%. M.p. 113–114 °C. FTIR (KBr pellet, cm^{-1}): 3063, 3034, 2210, 1590, 1509, 1490, 1283, 754, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.86 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 9.2 Hz, 2H), 7.52–7.41 (m, 4H), 7.32–7.26 (m, 4H), 7.14–7.07 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.2 (CH), 147.4 (C), 140.1 (C), 133.6 (C), 130.0(C), 129.7 (CH), 129.6 (CH), 129.2 (CH), 128.7 (CH), 125.3 (CH), 124.9 (CH), 123.7 (CH), 122.7 (CH), 118.8 (C), 110.0 (C). MS m/z: 373 (M + 1). Anal. Calcd for $C_{27}H_{20}N_2$: C, 87.07; H, 5.41; N, 7.52. Found: C, 87.10; H, 5.40; N, 7.52.

*2.3.2.2. (Z)-2-(4-(naphthalen-2-yl(phenyl)amino)phenyl)-3-phenylacrylonitrile (**2b**).* Yellow solid. Yield: 75%. M.p. 165–167 °C. FTIR (KBr pellet, cm^{-1}): 3063, 3033, 2216, 1627, 1594, 1508, 1490, 1294, 833, 812, 754, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.86 (d, J = 7.2 Hz, 2H), 7.77 (dd, J = 7.6 Hz, J = 9.2 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.50–7.37 (m, 6H), 7.33–7.28 (m, 4H), 7.18–7.09 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.7(CH), 147.0(C), 144.6 (C), 139.9 (C), 134.3 (C), 133.9(C), 130.4(C), 130.1(C), 129.5(CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 127.8 (CH), 127.6 (CH), 127.0 (CH), 126.8 (CH), 126.4 (CH), 125.1 (CH), 124.9 (CH), 124.6 (CH), 123.9 (CH), 122.8 (CH), 121.5 (CH), 118.1 (C), 111.1 (C). MS m/z: 423 (M + 1). Anal. Calcd for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.12; H, 5.25; N, 6.63.

*2.3.2.3. (Z)-2-(4-(diphenylamino)phenyl)-3-p-tolylacrylonitrile (**2c**).* Pale yellow solid. Yield: 80–82%. M.p. 124–125 °C. FTIR (KBr pellet, cm^{-1}): 3034, 2919, 2218, 1594, 1586, 1514, 1488, 1289, 1272, 839, 810, 749, 694.^{1}H NMR(400 MHz, $CDCl_3$) δ_H: 7.79 (d, J = 8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.41 (s, 1H), 7.32–7.26 (m, 6H), 7.15–7.07 (m, 8H), 2.42 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.6(CH), 147.0 (C), 140.1 (C), 139.9 (C), 131.2(C), 129.6(CH), 129.4(CH), 129.0 (CH), 127.8 (C), 126.6 (CH), 124.9 (CH), 123.6 (CH), 122.6(CH), 118.3 (C), 109.9 (C), 21.5(CH_3). MS m/z: 387 (M + 1). Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.02; H, 5.74; N, 7.20.

*2.3.2.4. (Z)-2-(4-(naphthalen-2-yl(phenyl)amino)phenyl)-3-p-tolylacrylonitrile (**2d**).* Pale yellow solid. Yield: 72–75%. M.p. 217–218 °C. FTIR (KBr pellet, cm^{-1}): 3047, 2914, 2216, 1627, 1594, 1508, 1490, 812, 754, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77 (dd, J = 6.8 Hz, J = 8.4 Hz, 4H), 7.62 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.49 (s, 1H), 7.42–7.38 (m, 3H), 7.33–7.27 (m, 5H), 7.16–7.10 (m, 5H), 2.40 (s, 3H). ^{13}C NMR

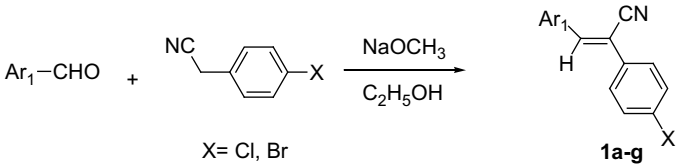
(400 MHz, $CDCl_3$): δ_c: 148.5 (CH), 147.0 (C), 144.6 (C), 140.6 (C), 140.0(C), 134.3 (C), 131.2 (C), 130.4 (C), 129.6 (CH), 129.4 (CH), 129.1 (CH), 129.0 (CH), 128.1(C), 127.5(CH), 127.0 (CH), 126.7 (CH), 126.4 (CH), 125.0 (CH), 124.9 (CH), 124.6(CH), 123.8 (CH), 122.9 (CH), 121.4 (CH), 118.2 (C), 110.0 (C), 21.5(CH_3). MS *m/z*: 437 (M + 1). Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.03; H, 5.52; N, 6.41.

*2.3.2.5. (Z)-2-(4-(diphenylamino)phenyl)-3-(naphthalen-1-yl)acrylonitrile (**2e**).* Yellow solid. Yield: 67–70%. M.p. 187–188 °C. FTIR (KBr pellet, cm^{-1}): 3056, 2216, 1608, 1586, 1506, 1487, 1285, 1271, 831, 778, 749, 695. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.17 (s, 1H), 8.07 (d, J = 7.2 Hz, 1H), 8.00 (dd, J = 3.6 Hz, J = 5.2 Hz, 1H), 7.93 (dd, J = 7.6 Hz, J = 6.8 Hz, 2H), 7.64–7.55 (m, 5H), 7.32 (dd, J = 8.0 Hz, J = 8.0 Hz, 4H), 7.18–7.06 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.0 (CH), 147.0 (C), 137.7 (C), 133.4 (C), 131.5 (C), 131.4 (C), 130.3 (C), 129.4 (CH), 128.9 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.3 (CH), 125.5 (CH), 125.0 (CH), 123.8 (CH), 123.4 (CH), 122.4 (CH), 117.8 (C), 114.7 (C). MS *m/z*: 423 (M + 1). Anal. Calcd for $C_{31}H_{22}N_2$: C. 88.12; H, 5.25; N, 6.63. Found: C, 88.16; H, 5.25; N, 6.62.

*2.3.2.6. (Z)-3-(naphthalen-1-yl)-2-(4-(phenyl(m-tolyl)amino)phenyl) acrylonitrile (**2f**).* Pale yellow solid. Yield: 60–62%. Mp. 125–126 °C. FTIR (KBr pellet, cm^{-1}): 3034, 2919, 2213, 1600, 1590, 1508, 1488, 1332, 1317, 1282, 1248, 1189, 838, 813, 780, 762, 703. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.16 (s, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.98 (dd, J = 4.4 Hz, J = 4.4 Hz, 1H), 7.94–7.91 (m, 2H), 7.63–7.55 (m, 5H), 7.32 (dd, J = 8.8 Hz, J = 6.8, 2H), 7.26 (s, 1H), 7.23–7.09 (m, 5H), 7.00–6.93 (m, 3H), 2.29 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.1 (CH), 147.1 (C), 146.9 (C), 139.4 (C), 137.6 (C), 133.4 (C), 131.5 (C), 131.4 (C), 130.3 (C), 129.4 (CH), 129.2 (CH), 128.9 (CH), 127.0 (CH), 126.9 (CH), 126.9 (CH), 126.8 (CH), 126.3 (CH), 125.8 (CH), 125.5 (CH), 125.0 (CH), 124.8 (CH), 123.6 (CH), 123.4 (CH), 122.4 (CH), 122.3 (CH), 117.8 (C), 114.8 (C), 21.36 (CH_3). MS *m/z*: 437 (M + 1). Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.04; H, 5.53; N, 6.44.

*2.3.2.7. (Z)-3-(naphthalen-1-yl)-2-(4-(naphthalen-1-yl(phenyl)amino)-phenyl)acrylonitrile (**2g**).* Pale yellow solid. Yield: 58–60%. M.p. 100–102 °C. FTIR (KBr pellet, cm^{-1}): 3058, 2210, 1607, 1591, 1507, 1491, 1295, 1274, 1249, 801, 777, 697. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.10 (s, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.96–7.88 (m, 5H), 7.82 (d, J = 8 Hz, 1H), 7.57–7.47 (m, 7H), 7.42–7.37 (m, 2H), 7.28–7.14 (m, 2H), 7.16 (d, J = 8 Hz, 2H), 7.05–7.00 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.5 (CH), 147.3 (C), 142.6 (C), 137.2 (C), 135.2 (C), 133.4 (C), 131.5 (C), 131.4 (C), 131.0 (C), 130.2 (C), 129.3 (CH), 128.8 (CH), 128.5 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.3 (CH), 126.2 (CH), 125.5 (CH), 123.9 (CH), 123.4 (CH), 123.2 (CH), 123.1 (CH), 123.0 (CH), 120.2 (CH), 119.4 (CH), 117.8 (C), 114.8 (C). MS *m/z*: 473 (M + 1). Anal. Calcd for $C_{35}H_{24}N_2$: C, 88.95; H, 5.12; N, 5.93. Found: C, 88.93; H, 5.11; N, 5.94.

*2.3.2.8. (Z)-3-(naphthalen-1-yl)-2-(4-(naphthalen-2-yl(phenyl)amino)-phenyl)acrylonitrile (**2h**).* Pale yellow solid. Yield: 62–65%. M.p. 133–134 °C. FTIR (KBr pellet, cm^{-1}): 3056, 3027, 2216, 1628, 1593, 1490, 1289, 839, 812, 783, 749, 698. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.19 (s, 1H), 8.08 (d, 1H), 8.01 (dd, J = 4 Hz, J = 5.2 Hz, 1H), 7.96–7.92 (m, 2H), 7.82–7.78 (m, 2H), 7.66 (d, J = 8.4 Hz, 3H), 7.61–7.54 (m, 4H), 7.47–7.40 (m, 2H), 7.35 (dd, J = 7.6 Hz, J = 8 Hz, 3H), 7.21 (dd, J = 6.4 Hz, J = 6.4 Hz, 4H), 7.15 (dd, J = 7.6 Hz, J = 7.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.9 (CH), 147.0 (C), 144.6 (C), 137.8 (C), 134.3 (C), 133.4 (C), 131.5 (C), 131.4 (C), 130.5 (C), 130.4 (C), 129.5 (CH), 129.2 (CH), 128.9 (CH), 127.6 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.4 (CH), 126.3 (CH), 125.5 (CH), 125.1 (CH), 124.9 (CH), 124.6 (CH), 123.9 (CH), 123.4 (CH), 122.8 (CH), 121.6 (CH), 117.8 (C), 114.7 (C). MS *m/z*: 473 (M + 1). Anal. Calcd for $C_{35}H_{24}N_2$: C, 88.95; H 5.12; N 5.93. Found: C, 88.97; H, 5.13; N, 5.94.



Ar_1= Phenyl, *p*-Tolyl, 1-Naphthyl, 2-Naphthyl, 9-Anthryl

Scheme 1. Synthesis of α, β-diarylacrylonitrile halides (**1a**–**1g**).

*2.3.2.9. (Z)-2-(4-(diphenylamino)phenyl)-3-(naphthalen-2-yl)acrylonitrile (**2i**).* Pale yellow solid. Yield: 78%. M.p. 154–155 °C. FTIR (KBr pellet, cm^{-1}): 3055, 3031, 2212, 1590, 1508, 1488, 1329, 1279, 910, 836, 819, 751, 695. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (s, 1H), 8.07 (d, J = 8 Hz, 1H), 7.92–7.85 (m, 3H), 7.59–7.53 (m, 5H), 7.31 (dd, J = 7.6 Hz, J = 7.2 Hz, 4H) 7.17–7.09 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.8 (CH), 147.0 (C), 139.7 (C), 133.9 (C), 133.1 (C), 131.6 (C), 129.9 (C), 129.4 (CH), 128.6 (CH), 128.5 (CH), 127.7 (CH), 127.4 (CH), 126.8 (CH), 126.7 (CH), 125.2 (CH), 125.1 (CH), 125.0 (CH), 123.7 (CH), 122.4 (CH), 118.1 (C), 111.2 (C). MS *m/z*: 423 (M + 1). Anal. Calcd for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.13; H, 5.25; N, 6.67.

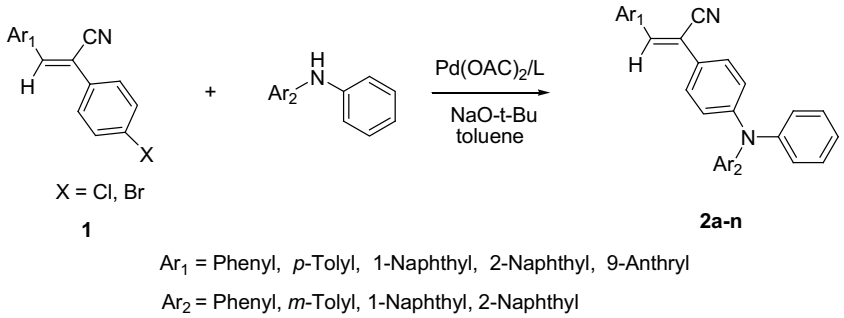
*2.3.2.10. (Z)-3-(naphthalen-2-yl)-2-(4-(phenyl(m-tolyl)amino)phenyl)acrylonitrile (**2j**).* Pale yellow solid. Yield: 75%. M.p. 149–150 °C. FTIR (KBr pellet, cm^{-1}): 3032, 2919, 2214, 1591, 1508, 1487, 908, 839, 818, 749, 697. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.25 (s, 1H), 7.06 (d, J = 8 Hz, 1H), 7.91–7.84 (m, 3H), 7.57–7.51 (m, 5H), 7.30 (dd, J = 8.4 Hz, J = 7.2 Hz, 2H), 7.19–7.08 (m, 6H), 6.97–6.91 (m, 3H), 2.29 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.1 (CH), 147.0 (C), 146.9 (C), 139.4 (C), 137.6 (C), 133.5 (C), 131.5 (C), 131.4 (C), 130.3 (C), 129.4 (CH), 129.2 (CH), 128.9 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.3 (CH), 125.8 (CH), 125.5 (CH), 125.0 (CH), 124.8 (CH), 123.6 (CH), 123.4 (CH), 122.3 (CH), 122.2 (CH), 117.8 (C), 114.7 (C), 21.36 (CH_3). MS *m/z*: 437 (M + 1). Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.08; H, 5.55; N, 6.42.

*2.3.2.11. (Z)-2-(4-(naphthalen-1-yl(phenyl)amino)phenyl)-3-(naphthalen-2-yl)acrylonitrile (**2k**).* Yellow solid. Yield: 65%. M.p. 175–176 °C. FTIR(KBr pellet, cm^{-1}): 3053, 2212, 1608, 1591, 508, 1491, 1392, 1294, 1273, 774, 747, 695. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 8.24 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.92–7.82 (m, 6H), 7.53–7.48 (m, 7H), 7.42–7.37 (m, 2H), 7.29–7.15 (m, 2H), 7.16 (d, J = 8 Hz, 2H), 7.06–7.00 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.3 (CH), 147.3 (C), 142.6 (C), 139.3 (C), 135.2 (C), 133.8 (C), 133.1 (C), 131.6 (C), 131.0 (C), 129.8 (C), 129.3 (CH), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.3 (CH), 126.2 (CH), 125.2 (CH), 123.9 (CH), 123.1 (CH), 123.0 (CH), 120.3 (CH), 118.3 (C), 111.2 (C). MS *m/z*: 473 (M + 1). Anal. Calcd for $C_{35}H_{24}N_2$: C, 88.95; H, 5.12; N, 5.93. Found: C, 88.96; H, 5.13; N, 5.94.

Table 1
Reaction conditions and yields of α, β-diarylacrylonitrile halides[a] (**1a**–**1g**).

Entry	Ar_1	X	Time(h)	Yields(%)
1a	Phenyl	Br	1	92
1b	*p*-Tolyl	Br	1	95
1c	1-Naphenyl	Br	2	93
1d	2-Naphenyl	Br	2	95
1e	9-Anphthyl	Br	3	89
1f	*p*-Tolyl	Cl	1	95
1g	1-Naphenyl	Cl	2	92

[a] Reaction conditions: 1.0 mmol of aromatic aldehydes, 1.0 mol of aromatic acetonitrile halides, 0.1 mmol of NaOMe, ethanol (10 ml), room temperature.



Scheme 2. Synthesis of compounds (**2a**–**2n**). Reactions run with 1.20 mmol of α, β-diarylacrylonitrile halide, 1.00 mmol of diarylamines, 1.50 mmol of sodium *tert*-butoxide, 0.06 mmol of palladium(II), and 0.18 mmol of P(*o*-tolyl)$_3$ in toluene at 110 °C for 8–24 h.

*2.3.2.12. (Z)-3-(naphthalen-2-yl)-2-(4-(naphthalen-2-yl(phenyl)amino)phenyl)acrylonitrile (**2l**).* Yellow solid. Yield: 67%. M.p. 235–237 °C. FTIR (KBr pellet, cm^{-1}): 3057, 2216, 1621, 1593, 1507, 1490, 1295, 1273, 902, 851, 815, 748, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (s, 1H), 8.07 (d, J = 8 Hz, 1H), 8.06–7.76 (m, 5H), 7.65–7.58 (m, 4H) 7.55–7.51 (m, 3H), 7.43–7.39 (m, 2H), 7.32–7.29 (m, 3H), 7.20–7.12 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.7 (CH), 147.0 (C), 144.6 (C), 139.9 (C), 134.3 (C), 133.9 (C), 133.1 (C), 131.5 (C), 130.4 (C), 130.0 (C), 129.5 (CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 125.2 (CH), 125.1 (CH), 124.9 (CH), 124.6 (CH), 123.9 (CH), 122.8 (CH), 121.5 (CH), 118.2 (C), 111.1 (C). MS m/z: 473 (M + 1). Anal. Calcd for $C_{35}H_{24}N_2$: C, 88.95; H, 5.12; N, 5.93. Found: C, 88.92; H, 5.16; N, 5.92.

*2.3.2.13. (Z)-3-(anthracen-9-yl)-2-(4-(diphenylamino)phenyl)acrylonitrile (**2m**).* Yellow solid. Yield: 76%. M.p. 185–190 °C. FTIR (KBr pellet, cm^{-1}): 3053, 2222, 1590, 1508, 1490, 1329, 1285, 887, 836, 755, 736, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.77 (s, 1H), 8.73 (s, 1H), 8.19–9.17 (m, 2H), 8.12–8.07 (m, 2H), 7.88–7.86 (m, 2H), 7.60–7.49 (m, 6H), 7.23–7.08 (m, 10H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 148.4 (CH), 147.0 (C), 146.6 (C), 138.9 (C), 131.2 (C), 129.5 (C), 129.2 (C), 128.9 (C), 128.3 (CH), 126.5 (CH), 125.5 (CH), 125.1 (CH), 125.0 (CH), 124.9 (CH), 123.9 (CH), 123.6 (CH), 122.4 (CH), 121.3 (CH), 118.9 (C). MS m/z: 473 (M + 1). Anal. Calcd for $C_{35}H_{24}N_2$: C, 88.95; H, 5.12; N, 5.93. Found: C, 88.94; H, 5.10; N, 5.90.

*2.3.2.14. (Z)-3-(anthracen-9-yl)-2-(4-(naphthalen-1-yl(phenyl)amino)phenyl)acrylonitrile (**2n**).* Yellow solid. Yield: 78%. M.p. 155–160 °C. FTIR (KBr pellet, cm^{-1}): 3053, 2216, 1624, 1593, 1507, 1490, 1294, 887, 842, 812, 746, 735, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.82 (s, 1H), 8.744 (s, 1H), 8.19 (dd, J = 4.8 Hz, J = 4 Hz, 2H), 8.11–8.09 (m, 2H), 7.94–7.88 (m, 4H), 7.79 (d, J = 8.4 Hz, 1H), 7.63–7.58 (m, 5H), 7.49–7.39 (m, 4H), 7.31 (d, J = 8.8 Hz, 1H), 7.20–7.17 (m, 5H). ^{13}C NMR (400 MHz, $CDCl_3$): δ_c: 149.2 (CH), 147.0 (C), 144.6 (C), 137.4 (C), 134.3 (C), 131.2 (C), 130.5 (C), 129.6 (C), 129.5 (C), 129.3 (C), 129.0 (CH), 128.7 (CH), 128.1 (CH), 127.6 (CH), 127.0 (CH), 126.6 (CH), 126.5 (CH), 125.4 (CH), 125.2 (CH), 125.1 (CH), 125.0 (CH), 124.7 (CH), 124.0 (CH), 122.8 (CH), 121.8 (CH), 121.6 (CH), 120.6 (CH),118.9 (C), 116.6 (C). MS m/z: 523 (M + 1). Anal. Calcd for $C_{39}H_{26}N_2$: C, 89.63; H, 5.01; N 5.36. Found: C, 89.65; H, 5.02; N, 5.38.

3. Results and discussion

3.1. Synthesis

The target compounds studied in this paper were prepared via a two-step procedure. α, β-Diarylacrylonitrile halides were prepared from aromatic aldehydes and arylacetonitrile halides with 10% NaOMe. The yields were consistently in the 90–95% range. The process of synthesis and yields is shown in Scheme 1 and Table 1.

And for the second step, the diarylamines reacted with α, β-diarylacrylonitrile halides to afford triphenylamine derivatives by the catalysis of Pd(OAc)$_2$/P(*o*-tolyl)$_3$ at 110 °C in toluene. The route to the synthesis of triphenylamine derivatives with α, β-diarylacrylonitrile (**2a**–**2n**) is presented in Scheme 2.

To the best of our knowledge, aryl C–N bond construction can be obtained either by the copper-catalyzed Ullmann condensation [24,25] or palladium-catalyzed cross-coupling reactions [26–29]. Palladium-catalyzed amination of aryl halides has been the focus of intensive research [30–32]. The use of a Pd/P(t-Bu)$_3$ catalyst system was first reported by Koie, and a modified system was used by Yamamoto to efficiently couple diarylamines with aryl halides to prepare triarylamines [29]. This work typified by methods developed by Buchwald and Hartwig had a major impact on aromatic C–N bond formation in academics [33–36]. In this work, we used the catalytic system of Pd/P(*o*-tolyl)$_3$ to prepare a variety of triphenylamines by the coupling of diarylamines with α, β-diarylacrylonitrile bromide and chloride (**1**), because P(*o*-tolyl)$_3$ as ligand was much more air stable than P(t-Bu)$_3$. The coupling of α, β-diarylacrylonitrile halides with diphenylamine, 3-methyldiphenylamine, N-phenyl-2-naphthylamine and N-phenyl-1-naphthylamine were studied. The results are summarized in Tables 2 and 3.

In subsequent experiments, we have observed that diarylamines react faster with aryl bromide relative to aryl chloride. Although the rate of oxidative addition of an aryl bromide to a Pd complex is faster than that of the corresponding aryl chloride, in some cases the reaction of the aryl chloride can be competitive with the reaction of the aryl bromide from their yields. Here, a specific class of novel triphenylamines from α, β-diarylacrylonitrile bromide and chloride was synthesized respectively.

Starburst molecules having a triarylamine core have improved thermal stability [8]. The thermal properties of these compounds were investigated by TGA. A typical TGA curve shows thermal stability up to 343–405 °C, which makes them potential emitters for organic light emitting device materials (Table 4); some representative data is shown in Fig. 1.

3.2. Photophysical properties

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

The UV absorption spectra in CH_2Cl_2 are shown in Fig. 2. The absorption behaviors are quite similar to each other, these derivatives reveal a common low-energy broad band at 350–450 nm assigned to the π–π* transitions of the compounds. The absorption

Table 2
Reactions of α, β-diarylacrylonitrile bromides with diarylamines catalyzed by $Pd(OAC)_2/P(o\text{-}tolyl)_3$.

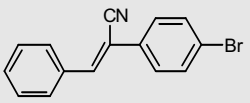
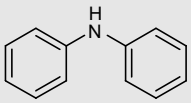
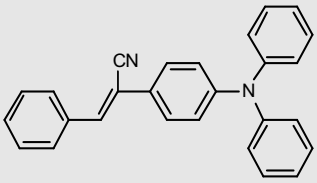
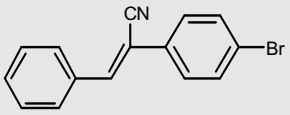
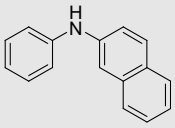
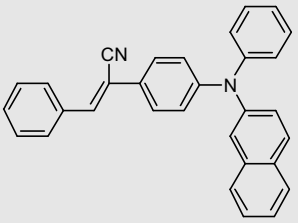
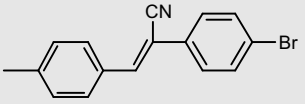
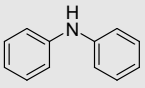
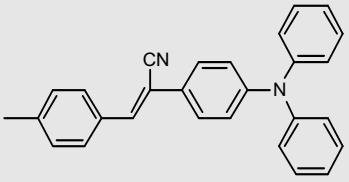
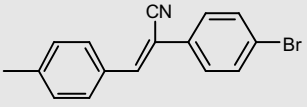
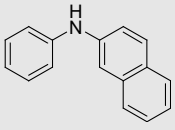
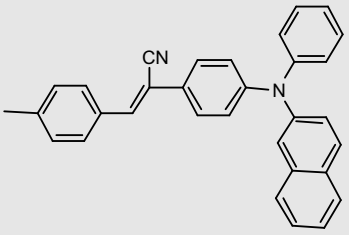
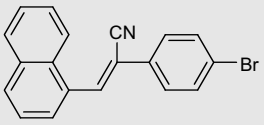
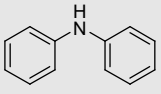
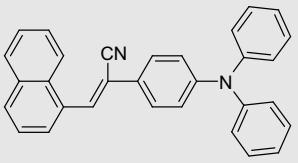
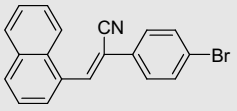
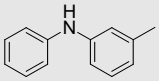
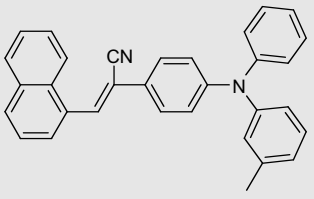
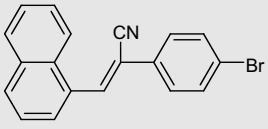
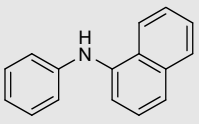
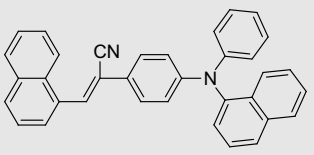
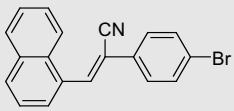
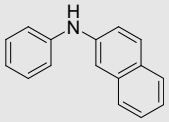
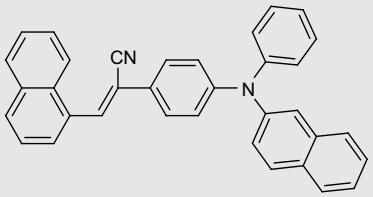
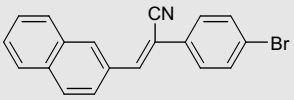
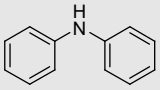
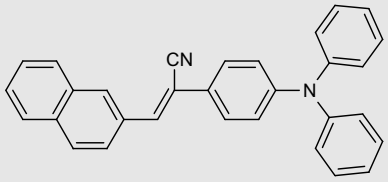
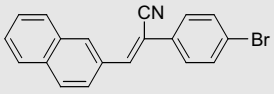
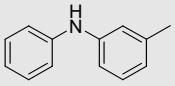
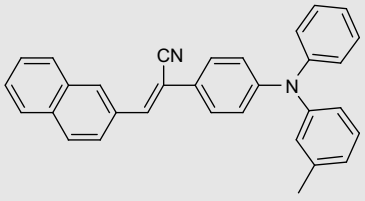
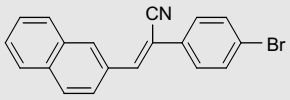
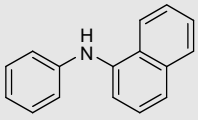
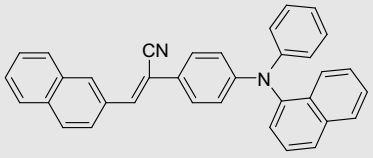
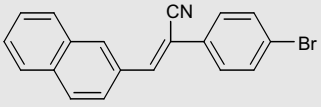
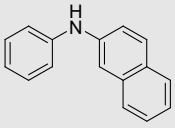
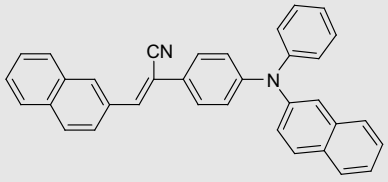
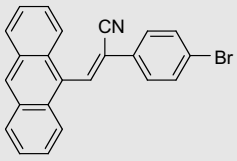
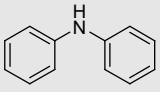
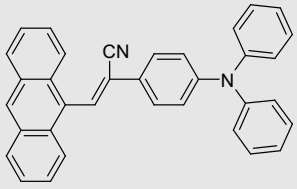
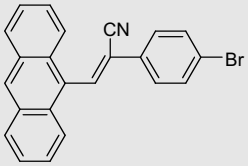
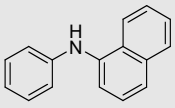
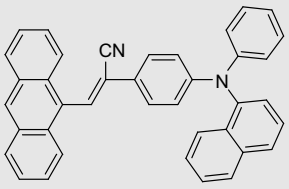
Entry	Aryl bromide	Diarylamine	Product		Yield (%)
1				**2a**	85
2				**2b**	75
3				**2c**	82
4				**2d**	72
5				**2e**	70
6				**2f**	60
7				**2g**	58

Table 2 (*continued*)

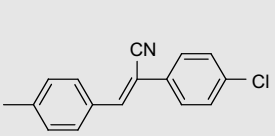
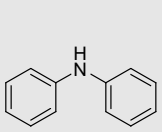
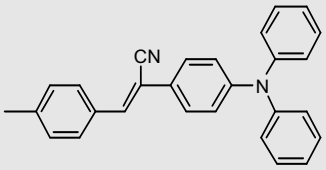
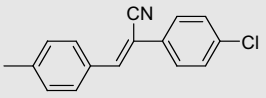
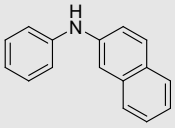
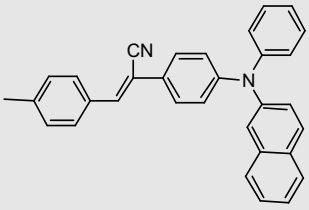
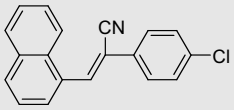
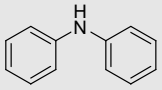
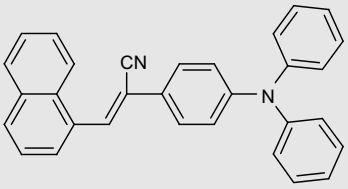
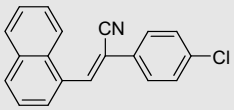
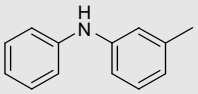
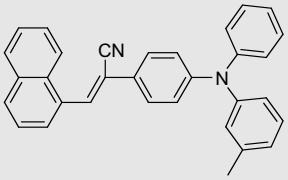
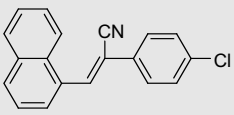
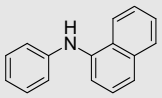
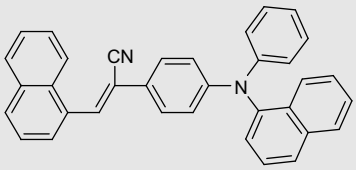
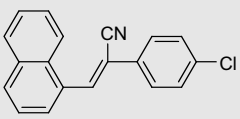
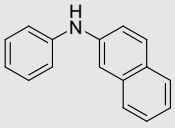
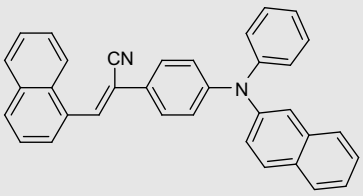
Entry	Aryl bromide	Diarylamine	Product		Yield (%)
8				**2h**	65
9				**2i**	78
10				**2j**	75
11				**2k**	65
12				**2l**	67
13				**2m**	76
14				**2n**	78

bands at 280–350 nm come from the combination of the n–π^* transition of triphenylamine moieties and the π–π^* transitions of the substituted aryl groups.

As is typical of charge–transfer transition, an increase in the polarity of the medium leads to a stokes shift of the absorption maximum. A change of solvent from CH_2Cl_2 to THF resulted in a little red shift (<10 nm) of the absorption maximum (Table 4), some representative spectra are shown in Fig. 3.

Photoluminescent spectra of the systems were also recorded in two solvents of different polarity. For the emission spectra in CH_2Cl_2

Table 3
Reactions of α, β-diarylacrylonitrile chlorides with diarylamines catalyzed by $Pd(OAC)_2/P(o\text{-}tolyl)_3$.

Entry	Aryl chloride	Diarylamine	Product	Yield (%)
1				80
2				75
3				67
4				62
5				60
6				62

solution, as show in Fig. 4, all of the compounds display similar behaviors and yield green emission at room temperature. The emission peaks of compounds are located at about 523–574 nm. We found when Ar_1 is 9-anphthyl and Ar_2 is 1-naphenyl (**2n**), the emission peak is obviously red-shifted by 51 nm from that compound **2c**.

Fig. 5 outlines the emission spectra of the compounds in solid state. All of the compounds exhibit green emission with a maximum peak at 500–570 nm. Compounds **2l**–**2n** have the emission maxima in the green region, close to yellow light. The emission peaks of the compounds in solid state show blue shifted 2–31 nm from those in CH_2Cl_2 solution except **2e**, indicating intermolecular interactions in their solid state. The fluorescence quantum efficiencies of compounds (**2a**–**2n**) were determined in tetrahydrofuran (Table 4). Their Φ_f is between 3.6 and 14.6%. The emission wavelength of each compound in CH_2Cl_2 solution appears longer than that in THF solution; this is evident from the data presented in Table 4. A change of solvent from CH_2Cl_2 to THF resulted in about 20 nm blue shift of the emission maximum. The polarity of the solvent plays an important role on the photophysical properties in such strong donor–acceptor system.

Table 4
Physical properties of compounds (**2a–2n**).

Entry	T_m[a] [°C]	T_d[a] [°C]	CH_2Cl_2 λ_{abs} [nm]	THF λ_{abs} [nm]	CH_2Cl_2 λ_{em} [nm]	THF λ_{em} [nm]	Solid λ_{em} [nm]	Φ_f[b] [%]
2a	113	343.2	301, 395	311, 397	534	514	508	11.2
2b	166	386.3	302,.398	313, 402	546	525	521	8.8
2c	124	346.2	299, 393	305, 398	523	503	513	14.6
2d	217	370.2	310, 398	315, 401	535	514	512	13.7
2e	187	376.8	300, 396	307, 400	549	530	554	13.3
2f	125	374.5	300, 397	308, 403	553	540	526	12.1
2g	101	392.3	257, 391	263, 395	544	529	531	7.6
2h	133	403.2	318, 399	322, 404	556	545	525	8.2
2i	154	376.4	302, 406	308, 412	541	526	499	14.5
2j	149	385.6	303, 409	309, 413	548	531	499	11.9
2k	175	402.3	269, 402	275, 404	538	518	536	9.9
2l	236	399.2	315, 410	320, 412	551	539	543	9.7
2m	186	405.5	298, 393	305, 403	566	551	560	3.6
2n	156	398.4	317, 395	324, 401	574	565	571	3.9

[a] Melting and decomposition temperature.
[b] Relative quantum yields (with fluorescein in THF $\Phi_f = 0.93$ as a standard).

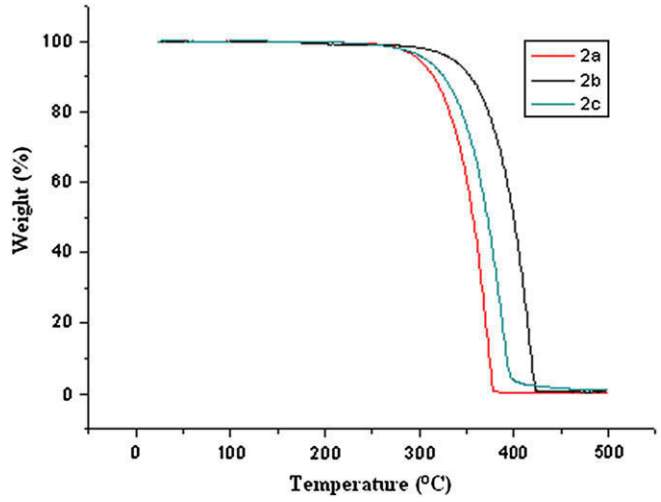


Fig. 1. The TGA spectrum of compounds (**2a–2c**).

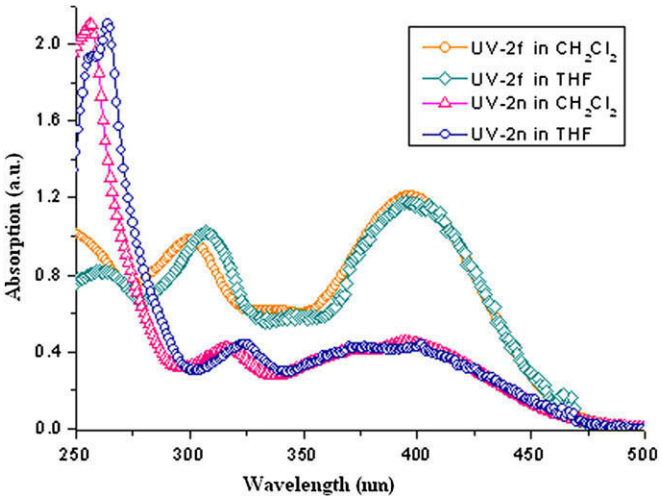


Fig. 3. Absorption spectra of compounds (**2f**, **2n**) in different solvents.

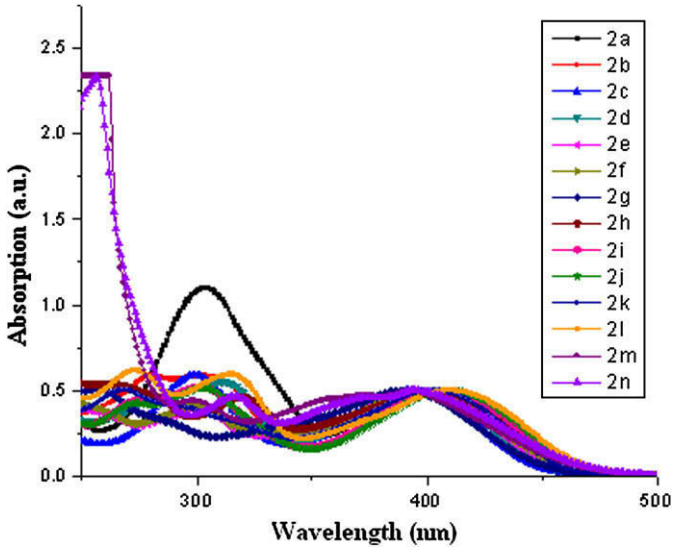


Fig. 2. Absorption spectra of compounds (**2a–2n**) in CH_2Cl_2 solution.

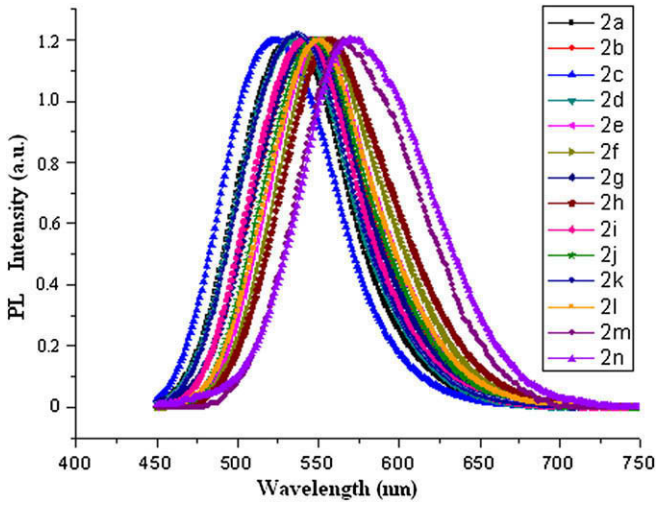


Fig. 4. PL spectra of compounds (**2a–2n**) in CH_2Cl_2 solution.

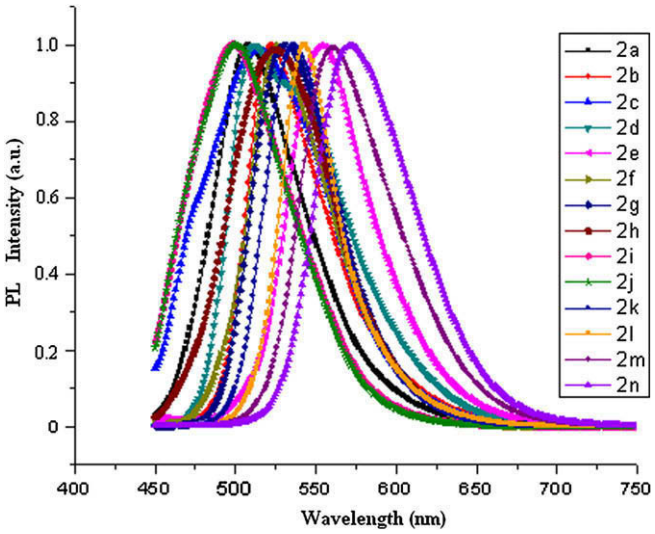


Fig. 5. PL spectra of compounds (**2a**–**2n**) in solid state.

4. Conclusions

In conclusion, a series of novel triphenylamine derivatives with α, β-diarylacrylonitrile were synthesized by the catalysis of Palladium in this paper. The absorption and photoluminescent spectra of these derivatives in CH_2Cl_2 and THF were investigated. These compounds displayed a Stokes shift in polar solvents. These compounds exhibit similar absorption and emission behaviors and emit strongly in solution and solid state, with the emission maxima in the range of 500–574 nm.

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] Burroughes JH, Bradley DDC, Broun AR, Marks RN, Mackay K, Friend RH, et al. Light-emitting diodes based on conjugated polymers. Nature 1990;347:539–41.
[3] Kulkarni AP, Tonzola CJ, Babel A, Jenekhe SA. Electron transport materials for organic light-emitting diodes. Chemistry of Materials 2004;16:4556–73.
[4] Ning ZJ, Chen Z, Zhang Q, Yan YL, Qian SX, Cao Y, et al. Aggregation-induced emission (AIE)-active starburst triarylamine fluorophores as potential non-doped red emitters for organic light-emitting diodes and Cl_2 gas chemodosimeter. Advanced Functional Materials 2007;17(18):3799–807.
[5] Liang M, Xu W, Cai FS, Chen PQ, Peng B, Chen J, et al. New triphenylamine-based organic dyes for efficient dye-sensitized solar cells. The Journal of Physical Chemistry C 2007;111(11):4465–72.
[6] Tian HN, Yang XC, Chen RK, Zhang R, Anders Hagfeldt, Licheng Sun. 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.
[7] Ning ZJ, Zhang Q, Wu WJ, Pei HC, Liu B, Tian H. Starburst triarylamine based dyes for efficient dye-sensitized solar cells. Journal of Organic Chemistry 2008;73(10):3791–7.
[8] Zheng RH, Häussler M, Dong HC, Lam JWY, Tang BZ. Synthesis, structural characterization, and thermal and optical properties of hyperbranched poly(aminoarylene)s. Macromolecules 2006;39(23):7973–84.
[9] 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.
[10] Shirota Y. Organic materials for electronic and optoelectronic devices. Journal of Materials Chemistry 2000;10:1–25.
[11] Shirota Y. Photo- and electroactive amorphous molecular materials molecular design, syntheses, reactions, properties, and applications. Journal of Materials Chemistry 2005;15:75–93.
[12] Thelakkat M. Star-shaped, dendrimeric and polymeric triarylamines as photoconductors and hole transport materials for electro-optical applications. Macromolecular Materials and Engineering 2002;287:442–61.
[13] 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.
[14] D'Sa BA, Kisanga P, Verkade JG. Direct synthesis of alpha, beta- unsaturated nitriles catalyzed by nonionic superbases. Journal of Organic Chemistry 1998;63:3961–7.
[15] 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.
[16] 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.
[17] 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.
[18] 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.
[19] Wienk MM, Janssen RAJ. High-spin cation radicals of meta-para aniline oligomers. Journal of the American Chemical Society 1997;119(19):4492–501.
[20] Kim YK, Shin DC, Kim SH, Ko CH, Yu HS, Chae YS, et al. Novel blue emitting material with high color purity. Advanced Materials 2001;13:1690–3.
[21] Yeh HC, Yeh SJ, Chen CT. Readily synthesised arylamino fumaronitrile for non-doped red organic light-emitting diodes. Chemical Communication 2003:2632–3.
[22] Huang PH, Shen JY, Pu SC, Wen YS, Lin JT, Chou PT, et al. Synthesis and characterization of new fluorescent two-photon absorption chromophores. Journal of Materials Chemistry 2006;16:850–7.
[23] Vaccaro W, Amore C, Berger J, Burrier R, Clader J, Davis H, et al. Inhibitors of acyl CoA: cholesterol acyltransferase. Journal of Medicinal Chemistry 1996;39:877–85.
[24] Paine AJ. Mechanisms and models for copper mediated nucleophilic aromatic substitution. 2. Single catalytic species from three different oxidation states of copper in an Ullmann synthesis of triarylamines. Journal of the Americal Chemical Society 1987;109(5):1496–502.
[25] Zapf A, Beller M. The development of efficient catalysts for palladium-catalyzed coupling reactions of aryl halides. Chemical Communications 2005:431–40.
[26] Harkal S, Rataboul F, Zapf A, Fuhrmann C, Riermeier T, Monsees A, et al. Dialkylphosphinoimidazoles as new ligands for palladium-catalyzed coupling reactions of aryl chlorides. Advanced Synthesis & Catalysis 2004;346:1742–8.
[27] Zapf A, Jackstell R, Rataboul F, Riermeier T, Monsees A, Fuhrmann C, et al. Practical synthesis of new and highly efficient ligands for the Suzuki reaction of aryl chlorides. Chemical Communications 2004:38–9.
[28] Michalik D, Kumar K, Zapf A, Tillack A, Arlt M, Heinrich T, et al. A short and efficient synthesis of N-aryl- and N-heteroaryl-N-(arylalkyl) piperazines. Tetrahedron Letters 2004;45:2057–61.
[29] Yamamoto T, Nishiyama M, Koie Y. Palladium-catalyzed synthesis of triarylamines from aryl halides and diarylamines. Tetrahedron Letters 1998;39:2367–70.
[30] Wolfe JP, Buchwald SL. A highly active catalyst for the room-temperature amination and Suzuki coupling of aryl chlorides. Angewandte Chemie International Edition 1999;38(16):2413–6.
[31] 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. Journal of Organic Chemistry 2000;65:1158–74.
[32] Hartwig JF. Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: scope and mechanism. Angewandte Chemie International Edition 1998;37:2046–67.
[33] Hartwig JF, Kawatsura M, Hauck SI, Shaughnessy KH, Alcazar-Roman LM. Room temperature palladium-catalyzed amination of aryl bromides and chlorides and extended scope of aromatic C–N bond formation with a commercial ligand. Journal of Organic Chemistry 1999;64(15):5575–80.
[34] 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.
[35] Huang XH, Anderson KW, Zim D, Jiang L, Klapars A, Buchwald SL. Expanding Pd-catalyzed C–N bond-forming processes: the first amidation of aryl sulfonates, aqueous amination, and complementarity with Cu-catalyzed reactions. Journal of the American Chemical Society 2003;125(22):6653–5.
[36] Biscoe MR, Fors BP, Buchwald SL. A new class of easily activated palladium precatalysts for facile C–N cross-coupling reactions and the low temperature oxidative addition of aryl chlorides. Journal of the American Chemical Society 2008;130(21):6686–7.