Synthesis and photophysical properties of novel thiophenylacrylonitrile derivatives containing a triphenylamine moiety

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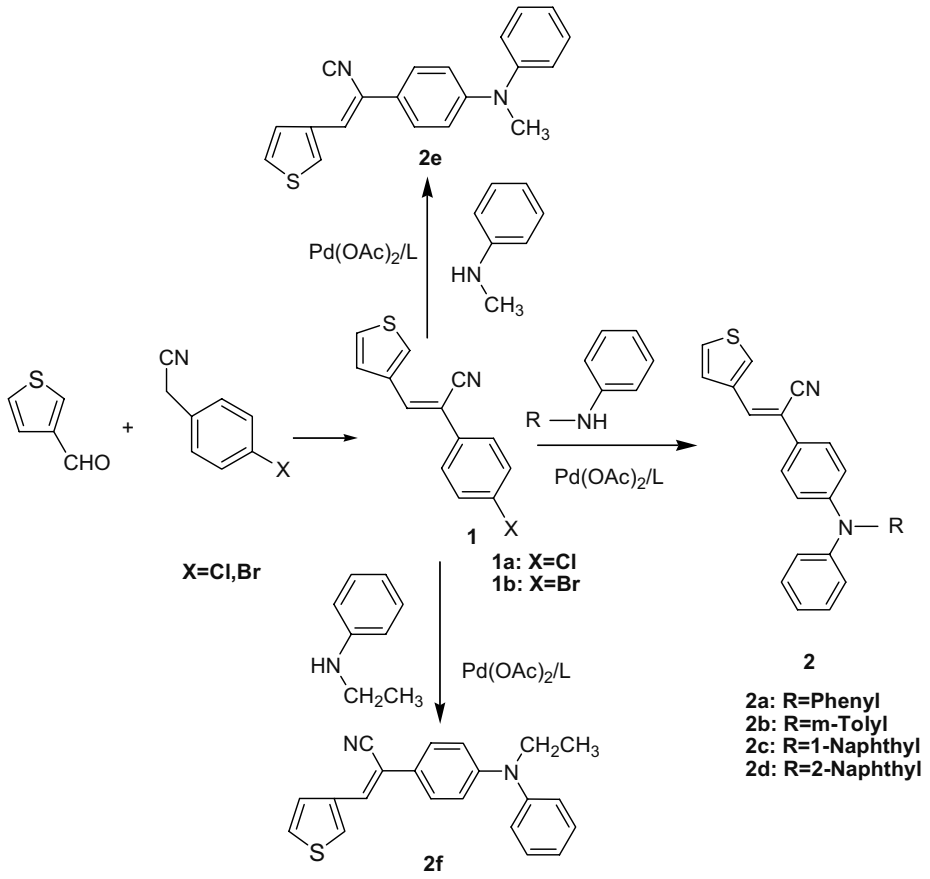
(*Z*)-2-(4-Halogenophenyl)-3-(thiophen-3-yl)acrylonitrile can be prepared by condensation of thiophene-3-carbaldehyde with arylacetonitrile halides in the presence of catalytic amounts of $NaOCH_3$ at room temperature. Secondary arylamines reacted with (*Z*)-2-(4-halogenophenyl)-3-(thiophen-3-yl)acrylonitriles to afford thiophenyl-acrylonitrile derivatives containing a triphenylamine moiety on catalysis by $Pd(OAc)_2/P(o\text{-tolyl})_3$ at 120 °C in toluene. The UV-Vis absorption and photoluminescent (PL) spectra of the products in CH_2Cl_2 were investigated.

Keywords: thiophen, acrylonitrile, triphenylamine, aryl halides, Pd-catalysed

Thiophene chemistry[1] is well established and thiophene-based heterocycles are key intermediates and relevant targets in the fields of synthetic, medicinal and materials chemistry.[2,3] Recently, thiophenes and benzothiophenes have emerged as classes of molecules with synthetic utility[4] and a wide array of biological activities.[5-8] The high polarisability of sulfur atoms in thiophene rings leads to a stabilisation of the conjugated chain and to excellent charge-transport properties, which are one of the most crucial assets for applications in organic and molecular electronics.[9-11] At the same time, triphenylamine derivatives are important materials, widely used in organic photoconductor, organic light-emitting compounds,[12-15] organic solar cells and other fields due to their excellent electrochemical stability, electron-donating ability and optoelectronic properties.[16,17] Based on our studies in the field of triphenylamine[18-21] and acrylonitrile derivatives,[22] we became interested in the preparation of new thiophenylacrylonitrile derivatives containing the triphenylamine moeity. During the past few decades, Ullmann coupling[23,24] and palladium-catalysed coupling[12,13,25] reaction have been the main synthetic methods for triarylamines. We now report the synthesis of a series of novel thiophene derivatives containing the triphenylamine moiety via palladium-catalysed coupling.

The target compounds were obtained by condensation reactions and palladium-catalysed coupling reactions. (*Z*)-2-(4-Halogenophenyl)-3-(thiophen-3-yl) acrylonitriles were synthesised according to the method previously reported.[26] Thiophenylacrylonitrile derivatives containing the triphenyl-amine moiety (**2a–f**) were obtained via C–N bond formation. The process of synthesis is shown in Scheme 1. Yields of products are listed in Table 1.



Scheme 1

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Table 1 Structures, reaction conditions and yields of thiophenylacrylonitrile derivatives

Product	R	X	Time/h	Yields/%
2a	Phenyl	Br	16	66
2a	Phenyl	Cl	18	53
2b	*m*-Tolyl	Br	18	70
2b	*m*-Tolyl	Cl	19	65
2c	1-Naphthyl	Br	20	63
2c	1-Naphthyl	Cl	24	60
2d	2-Naphthyl	Br	18	75
2d	2-Naphthyl	Cl	20	70
2e	Methyl	Br	14	72
2e	Methyl	Cl	17	68
2f	Ethyl	Br	14	75
2f	Ethyl	Cl	16	70

Table 2 Physical properties of thiophenylacrylonitrile derivatives

Entry	$^{a}\lambda_{max}^{abs}$ nm	$^{b}\lambda_{max}^{em}$ nm
2a	298, 395	522
2b	306, 401	523
2c	308, 402	531
2d	297, 391	517
2e	288, 402	533
2f	296, 390	516

[a]Maximum absorption wavelength in CH_2Cl_2.
[b]Maximum emission wavelength in CH_2Cl_2.

(*Z*)-2-(4-bromo- and chlorophenyl-3-(thiophen-3-yl)acrylonitriles can react with aromatic amines as in Table 1**,** the bromo compounds being more reactive**.**

We then investigated the photophysical properties of compounds **2**. The UV-Vis (Fig. 1) and PL spectra (Fig. 2) in dilute dichloromethane solution were recorded. All the compounds yield green emissions in solution at room temperature. We have observed from Fig. 1 that the absorption behaviours are quite similar to each other and these derivatives reveal a common low-energy broad band at 350–450 nm owing to the π–π* transitions of the compounds. The absorption bands at 280–350 nm attributed to the combination of the n–π* transition of triphenylamine moieties and the π–π* transitions of the thiophene groups.

For the emission spectra in dilute dichloromethane solutions, as shown in Fig. 2, all of the compounds display similar behaviour and yield green emission at room temperature. The emission peaks of compounds are located at about 515–533nm.

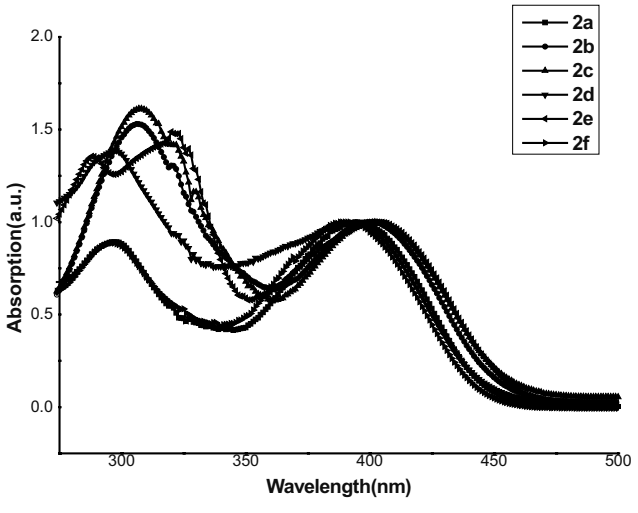

Fig.1 UV-Vis spectra of compounds **2** in CH_2Cl_2.

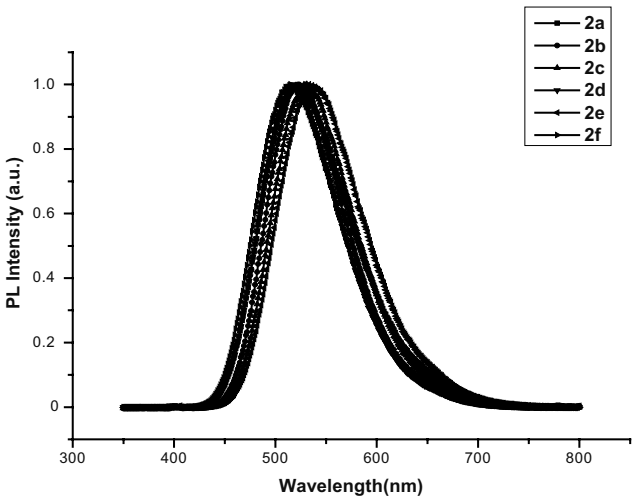

Fig. 2 PL spectra of compounds **2** in CH_2Cl_2.

Experimental

Aromatic amines, 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 other chemicals were used as supplied. All melting points were determined with a WRS-1A melting point apparatus and were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were run on a Bruker AV-400 NMR spectrometer and chemical shifts expressed as δ (ppm) values with TMS as internal standard. IR spectra were recorded in KBr on a Nicolet NEXUS 470 FT-IR spectrophotometer. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). Mass spectra were obtained on Varian 500-MS. Elemental analyses were determined with a Perkin–Elmer 240 analyser. UV-Vis spectra were recorded on a Hitachi U-3300 model while PL spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer.

General procedure for the synthesis of **(1a, 1b)**
A solution of the thiophene-3-carbaldehyde (10 mmol) and aromatic acetonitrile (10 mmol) in absolute EtOH (30 mL) was treated with NaOMe (1 mmol) portion wise, stirred at room temperature for 2–3 hours, cooled to 0 °C, and filtered. The precipitate was washed with EtOH.

(*Z)-2-(4-chlorophenyl)-3-(thiophen-3-yl)acrylonitrile* **(1a):** Yellow solid. Yield: 91%. M.p. 92–94 °C. FTIR (KBr pellet, cm^{-1}): 3092, 2209, 1601, 1491, 1417, 1341, 1097, 825, 775. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.66 (d, *J* = 1.8 Hz, 1H), 7.63 (s, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 6.0 Hz,1 H), 7.15 (dd, *J* = 4.0 Hz, *J* = 4.8 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 135.6, 135.4, 132.9, 132.1, 128.9, 127.1, 127.1, 126.58, 123.0, 118.2, 108.3. Anal. Calcd for $C_{13}H_8ClNS$: C, 63.54; H, 3.28; Cl, 14.43; N, 5.70; S, 13.05. Found: C, 63.50; H, 3.25; N, 5.69%.

(Z)-2-(4-bromophenyl)-3-(thiophen-3-yl)acrylonitrile **(1b):** Yellow solid. Yield: 90%. M.p. 88–90 °C FTIR (KBr pellet, cm^{-1}): 3097, 2207, 1602, 1488, 1415, 1336, 1076, 823, 779. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (d, *J* = 2.0 Hz, 1 H), 7.78 (d, *J* = 5.2 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.53 (s, 1 H), 7.51(d, *J* = 9.0 Hz, 2H) 7.40 (dd, *J* = 2.8 Hz, *J* = 2.8 Hz,1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c:135.8, 135.6, 133.1, 132.2, 129.9, 127.2, 127.2, 126.8, 123.1, 118.0, 108.7. Anal. Calcd for $C_{13}H_8BrNS$: C, 53.81; H, 2.78; Br, 27.54; N, 4.83; S, 11.05. Found: C, 53.74; H, 2.70; N,4.76%.

General procedure for the synthesis of thiophenylacrylonitrile derivatives **(2a–f)**
To a 25 mL sidearm flask under vacuum was added (*Z*)-2-(4-halogenophenyl)-3-(thiophen-3-yl) acrylonitrile (1.20 mmol), the aromatic amine (1.00 mmol), $Pd(OAc)_2$(0.06 mmol, Pd/Br = 5%), $P(o\text{-}tolyl)_3$(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 120 °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 ethyl acetate/cyclohexane (1/10 mixture) as eluents.

(Z)-2-(4-(diphenylamino)phenyl)-3-(thiophen-3-yl)acrylonitrile **(2a)**: Yellow solid. M.p. 82–84 °C. FTIR (KBr pellet, cm^{-1}): 3035, 2213, 1590, 1490, 1332, 1284, 1076, 828, 755, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (d, J = 2.4 Hz, 1 H), 7.77 (d, J = 4.8 Hz, 1 H), 7.58–7.54 (m, 1 H), 7.51 (d, J = 8.8 Hz, 2 H), 7.44 (s, 1 H), 7.41–7.40 (m, 1 H), 7.31–7.29 (m, 4 H), 7.15 (d, J = 8.0 Hz, 4 H), 7.11–7.08 (m, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 141.4, 137.3, 134.5, 134.1, 132.3, 132.2, 130.4, 129.8, 129.8, 129.4, 127.3, 127.1, 125.4, 123.7, 107.1. MS *m/z*: 379(M + 1). Anal. Calcd for $C_{25}H_{18}N_2S$: C, 79.33; H, 4.79; N, 7.40; S, 8.47. Found: C, 79.16; H, 4.72; N, 7.44%.

(Z)-2-[4-(phenyl-m-tolyl-amino)phenyl]-3-(thiophen-3-yl) acrylonitrile **(2b):** Yellow solid. M.p. 92–96 °C. FTIR (KBr pellet, cm^{-1}): 3033, 2913, 2856, 2204,1592, 1508, 1318, 1279, 1190, 833, 782. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (d, J = 2.4 Hz, 1 H), 7.79 (d, J = 5.2 Hz, 1 H), 7.52 (d, J = 8.4 Hz, 2 H), 7.45 (s, 1 H), 7.40–7.39 (m, 1 H), 7.34–7.30 (m, 2 H), 7.21 (d, J = 8.0 Hz, 1 H), 7.16 (d, J = 7.6 Hz, 2 H), 7.10 (d, J = 8.8 Hz, 3 H), 7.00 (s, 1 H), 6.96 (dd, J = 7.2 Hz, J = 7.2 Hz, 2 H), 2.30 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 142.3, 139.2, 138.3, 137.3, 136.3, 134.4, 133.8, 132.2, 131.3, 130.0, 130.0, 129.9, 129.8, 129.3, 128.8, 128.2, 127.7, 127.4, 125.3, 124.9, 109.2, 28.3. MS *m/z*: 393(M + 1). Calcd for $C_{26}H_{20}N_2S$: C, 79.56; H, 5.14; N, 7.14; S, 8.17. Found: C, 79.40; H, 5.28; N, 7.19%.

(Z)-2-[4-(naphthalen-1-yl-phenylamino)phenyl)-3-(thiophen-3-yl] acrylonitrile **(2c):** Yellow solid. M.p. 74–76 °C. FTIR(KBr pellet, cm^{-1}): 3035, 2216, 1592, 1506, 1316, 1269, 1190, 908, 837, 778, 754, 696, 755, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.92(d, J = 3.6 Hz, 1 H), 7.89 (d, J = 3.6 Hz, 1 H), 7.87 (d, J = 2.0 Hz, 1 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.74 (d, J = 5.2 Hz, 1 H), 7.50 (d, J = 8.0 Hz, 1 H), 7.49(s, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.39–7.35 (m, 4 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 7.6 Hz, 2 H), 7.04 (d, J = 7.6 Hz, 1 H), 6.98 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c:151.3, 150.5, 149.9, 148.3, 145.3, 139.3, 135.9, 133.2, 132.8, 132.1, 131.1, 130.64, 130.1, 129.4, 128. 8, 128.0, 127.3, 127.0, 126.4, 126.3, 125.7, 124.6, 123.6, 119.0, 108.6. MS *m/z*: 429(M + 1). Calcd for $C_{29}H_{20}N_2S$: C, 81.28; H,4.70; N, 6.54; S, 7.48. Found: C, 81.37; H, 4.59; N, 6.65%.

(Z)-2-[4-(naphthalen-2-yl-phenylamino)phenyl]-3-(thiophen-3-yl) Acrylonitrile **(2d):** Yellow solid. M.p. 143–145 °C. FTIR (KBr pellet, cm^{-1}): 3036, 2213, 1593, 1506, 1294, 1236, 1190, 908, 838, 750, 732, 659. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (d, J = 2.0 Hz, 1 H), 7.80 (d, J = 8.8 Hz, 2 H), 7.76 (d, J = 3.2 Hz, 1 H), 7.63 (d, J = 7.6 Hz, 1 H), 7.53 (d, J = 8.8 Hz, 3 H), 7.45 (s, 1 H), 7.44–7.39 (m, 3 H), 7.32–7.30 (m, 3 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.16 (s, 1 H), 7.14–7.11 (m, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 150.4, 149.3, 148.2, 147.3, 144.7, 138.5, 132.1, 131.2, 130.6, 129.7, 129.0, 127.9, 127.6, 127.1, 127.00, 126.6, 126.2, 125.7, 125.0, 124.2, 123.8, 123.1, 122.1, 118.8, 107.2. MS *m/z*: 429(M + 1). Calcd for $C_{29}H_{20}N_2S$: C, 81.28; H, 4.70; N, 6.54; S, 7.48. Found: C, 81.24; H, 4.71; N, 6.45%.

(*Z)-2-[4-(methylphenylamino)phenyl]-3-(thiophen-3-yl) acrylonitrile* **(2e):** Yellow solid. M.p. 82–84 °C.FTIR (KBr pellet, cm^{-1}): 3039, 2973, 2929, 2212, 1590, 1515, 1348, 1255, 1194, 1122, 821, 750, 700. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.85 (d, J = 2.8 Hz, 1 H), 7.75 (d, J = 4.0 Hz, 1 H), 7.52 (d, J = 8.8 Hz, 2 H), 7.39–7.36 (m, 4 H), 7.18 (d, J = 8.0 Hz, 2 H), 7.14 (dd, J = 7.2 Hz, J = 7.2 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 3.36 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 148.6, 147.1, 139.4, 133.2, 129.7, 129.3, 128.6, 127.0, 126.4, 125.2, 124.3, 123.3, 122.1, 122.0, 109.1, 46.88. MS *m/z*: 317(M + 1). Calcd for $C_{20}H_{16}N_2S$: C, 75.92; H, 5.10; N, 8.85; S, 10.13. Found: C, 75.83; H, 5.19; N, 8.80%.

(Z)-2-(4-(ethyl(phenyl)amino)phenyl)-3-(thiophen-3-yl) acrylonitrile **(2f):** Yellow solid. M.p. 84–86 °C. FTIR (KBr pellet, cm^{-1}): 3039, 2973, 2929, 2212, 1610, 1514, 1376, 1266, 1199, 1129, 822, 781, 699. ^{1}H NMR (400 MHz,$CDCl_3$) δ_H: 7.87 (d, J = 2.0 Hz, 1 H), 7.76 (d, J = 5.2 Hz, 1 H), 7.49 (s, 1 H),7.40 (s, 1H), 7.39–7.37 (m, 4 H), 7.19–7.17 (m, 3 H), 6.87 (d, J = 8.2 Hz, 2 H), 3.85–3.80 (m, 2 H), 1.26 (t, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 148.8, 147.2, 139.4, 133.0, 129.5, 129.1, 128.5, 127.3, 126.5, 125.8, 124.9, 123.6, 122.5, 122.3, 109.6, 48.0, 29.70. MS *m/z*: 331(M + 1). Calcd for $C_{21}H_{18}N_2S$: C, 76.33; H, 5.49; N, 8.48; S, 9.70. Found: C, 76.33; H, 5.50; N, 8.45%.

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