Synthesis and photophysical properties of novel biphenyl derivatives containing furan and thiophene groups

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(*Z*)-2-(4-Bromophenyl)-3-(furan-2-yl)acrylonitrile and (*Z*)-2-(4-bromophenyl)-3- (thiophen-2-yl)acrylonitrile were prepared by condensation of furan-2-carbaldehyde and thiophene-2-carbaldehyde with (4-bromophenyl)acetonitrile in the presence of catalytic amount of $NaOCH_3$ at room temperature. A series of novel biphenyl derivatives containing furan and thiophene groups was synthesised from (*Z*)-2-(4-bromophenyl)-3-(furan-2-yl)acrylonitrile and (*Z*)-2-(4-bromophenyl)-3- (thiophen-2-yl)acrylonitrile via Suzuki coupling to arylboronic acids. The structures of these compounds were characterised by FT-IR, ^{1}H NMR, ^{13}C NMR, and HRMS. The UV-Vis absorption and photoluminescence spectra of the novel compounds in CH_2Cl_2 solution were investigated.

Keywords: furan, thiophene, Suzuki reaction, Pd-catalysed coupling, acrylonitrile

Furan and thiophene chemistry has been studied for a long time.[1,2] Furan can be used for conducting polymers because of its superior electrochromic effect and good redox ability.[3,4] While thiophene-based heterocycles are key intermediates and relevant targets in the fields of synthetic, medicinal, and materials chemistry.[5,6] Furthermore, aromatic compounds based on biphenyls also play an important role in OLEDs as well as in dyes and pigments because of their easy synthesis and highly polarisable π-electron systems.[7,8]

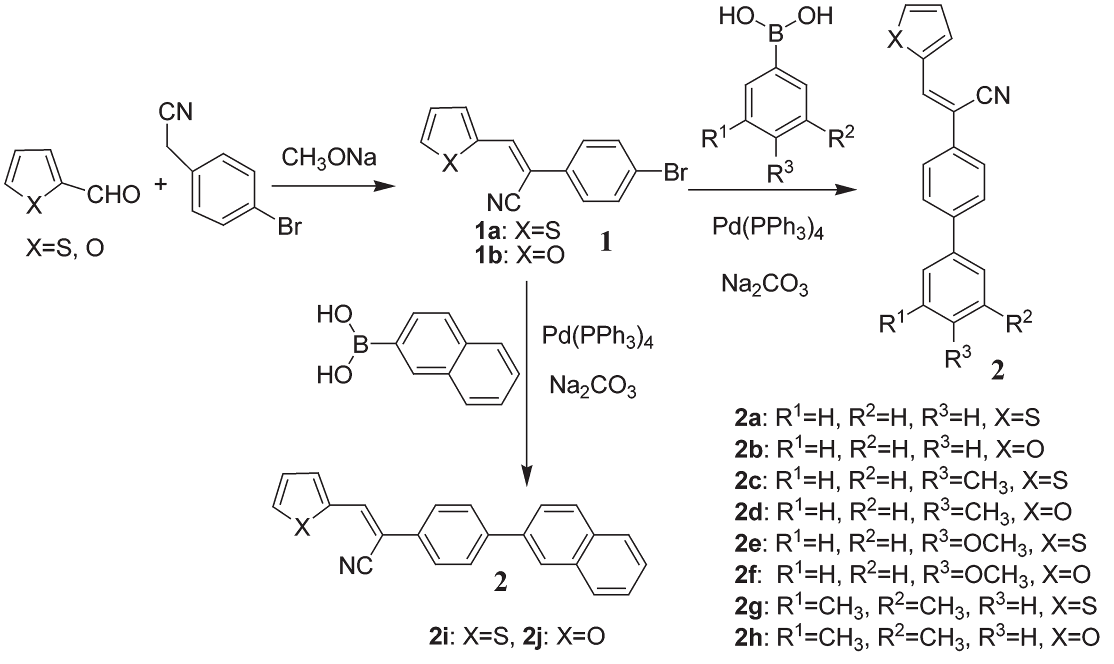
Based on our extensive studies in the field of organic light-emitting device materials as well as in palladium-catalysed coupling reactions,[9–11] we became interested in the preparation of new functional biphenyl derivatives containing furan and thiophene groups. We now report the design and synthesis of a series of novel biphenyl derivatives containing furan and thiophene rings and studied their photophysical properties as potential OLED materials.

The target compounds (**2a–j**) were obtained by a two-step procedure (Scheme 1). To the best of our knowledge, aryl C–C bond construction can be induced either by palladium catalysts or nickel catalysts.[12,13] Palladium-catalysed cross coupling reactions which are widely used to form C–C bonds are important reactions in organic synthesis.[14] In this work, we used the catalytic system of $Pd(PPh_3)_4$ to prepare compounds **2a–j**. The synthesis of (*Z*)-2-(4-bromophenyl)-3-(thiophen-2-yl) acrylonitrile and (*Z*)-2-(4-bromophenyl)-3-(furan-2-yl)acrylonitrile (**1a,1b**) were based on the previously reported literature.[15] For the second step, various substituted arylboronic acids were reacted with **1a** and **1b** to afford a series of novel biphenyl derivatives containing furan and thiophene rings by Suzuki reaction in the presence of the catalyst $Pd(PPh_3)_4$. The reaction times and yields are shown in Table 1.

In order to investigate their photophysical properties, the UV and PL spectra in dilute dichloromethane solution were recorded. All compounds yield blue emissions in solution at room temperature.

As indicated by the absorption spectra (Table 1), the absorption behaviour of **2a–j** were quite similar to each other, and most of them displayed two absorption peaks at about 255–268 nm and 357–363 nm which were ascribed to π–π* transitions.

For the emission spectra in dilute dichloromethane solutions, all of the compounds yield blue emission at room



Scheme 1 Synthesis of target compounds **2a–j**.

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Table 1 Reaction conditions, yields and photophysical properties of compounds **2a–j**

Entry	X	Time/h	Yield/%	${}^{a}\lambda_{max}^{abs}$/nm	${}^{b}\lambda_{max}^{em}$/nm	ε^{c}/mol·L^{-1}·cm^{-1}
2a	S	4	93	266, 358	436	13504, 19232
2b	O	4	95	255, 357	420	12314, 18199
2c	S	4	90	268, 360	433	13655, 19748
2d	O	4	94	257, 359	432	12887, 18201
2e	S	4	91	259, 359	431	14102, 19983
2f	O	4	94	255, 357	431	13251, 18793
2g	S	6	87	268, 360	444	13656, 19786
2h	O	6	92	255, 358	441	12784, 18910
2i	S	8	82	260, 363	445	14256, 21053
2j	O	8	89	**258, 362**	442	13470, 19483

[a] Maximum absorption wavelength in CH_2Cl_2.

[b] Maximum emission wavelength in CH_2Cl_2.

[c] Extinction coefficients determined in CH_2Cl_2 solutions when the concentration of each compound is 1.0×10^{-5} M.

temperature. The emission peaks of compounds are located at about 420–445 nm (Table 1).

Conclusion

In conclusion, several novel biphenyl derivatives containing furan and thiophene groups have been synthesised via the Suzuki reaction under mild conditions and in high yields. The absorption and photoluminescence spectra of the products in CH_2Cl_2 were investigated. These compounds exhibit similar absorption and emission behaviour and emit strongly in solution, with the emission maxima in the range of 420–445 nm.

Experimental

Boronic acid derivatives and tetrakis(triphenylphosphine)palladium (0) were purchased from Aldrich Chemical Co. Sodium carbonate was purchased from Alfa-Aesar and stored in a Vacuum Atmospheres glove box under nitrogen. All chemicals were used as supplied. All melting points were determined with a WRS-1A melting point apparatus and were uncorrected. Proton NMR (^{1}H NMR and ^{13}C NMR) spectra were run on a Bruker AV-400 NMR spectrometer in $CDCl_3$ and chemical shifts are expressed as δ (ppm) values with TMS as an 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 a Jeol JMS-SX102 A HRGC/LC/MS instrument operating in an electron-impact (EI) mode at 70 eV. UV-Vis spectra were recorded on a Hitachi U-3300 model while PL spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis of **(1a, 1b)**; *general procedure*

A solution of the thiophene-2-carbaldehyde or furan-2-carbaldehyde (1 mmol) and (4-bromophenyl)acetonitrile (1 mmol) in absolute EtOH (10 mL) was treated with NaOMe (0.1 mmol) portionwise, stirred at room temperature for 2–3 h, cooled to 0 °C, and filtered. The precipitate was washed with EtOH.

(Z)*-2-(4-Bromophenyl)-3-(thiophen-2-yl)acrylonitrile*[16] (**1a**): Yellow solid. Yield: 96%. M.p. 115–116 °C. (lit.[16] 118 °C) FTIR (KBr pellet, cm^{-1}): 3034, 2207, 1593, 1487, 1417, 1369, 1077, 824, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.67 (d, J = 3.6 Hz, 1H), 7.65 (s, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.55 (s, 1H), 7.50 (d, J = 8.8Hz, 2H), 7.15–7.17 (m, 1H).

(Z)*-2-(4-Bromophenyl)-3-(furan-2-yl)acrylonitrile* (**1b**): Yellow solid. Yield: 90%. M.p. 63–65 °C FTIR(KBr pellet, cm^{-1}): 3148, 3045, 2214, 1596, 1486, 1464, 1406, 1334, 1141, 1090, 1078, 1026, 1003, 931, 894, 822, 745, 591, 488. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.62 (d, J = 1.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.37 (s, 1H), 7.21 (d, J = 3.2 Hz, 1H), 6.60 (dd, J = 1.6 Hz, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 149.9, 145.2, 132.6, 132.2, 128.2, 127.0, 123.2, 117.4, 115.9, 113.0, 106.3. HRMS (EI): Calcd for $C_{13}H_8BrNO$: 272.9789. Found: 272.9787.

Synthesis of **2a–j;** *general procedure*

A degassed mixture of (*Z*)-2-(4-bromophenyl)-3-(furan-2-yl) acrylonitrile (1.0 mmol), Na_2CO_3 (2.2 mmol), water(1.1 mL), EtOH (0.8 mL), 1,2-dimethoxyethane (2.5 mL), the arylboronic acid (1.2 mmol), and $Pd(PPh_3)_4$ (0.01 mmol) was heated at reflux for the requisite time (Table 1). 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 **2a–j** [eluent: ethyl acetate-hexane (1:8)].

(Z)*-2-(Biphenyl-4-yl)-3- (thiophen-2-yl)acrylonitrile* (**2a**): Yellow solid. Yield: 93%. M.p. 139 °C. FTIR (KBr pellet, cm^{-1}): 3113, 3032, 2209, 1578, 1485, 1418, 1363, 1201, 1054, 839, 765,719. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.74–7.72 (m, 3H), 7.70–7.66 (m, 3H), 7.62 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 5.2 Hz, 1H), 7.47 (dd, J = 7.2 Hz, J = 8.0 Hz, 2H), 7.39 (dd, J = 7.2 Hz, J = 7.6 Hz, 1H), 7.17(dd, J = 3.6 Hz, J = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 141.7, 139.9, 138.0, 133.8, 132.8, 132.4, 130.0, 128.9, 127.8, 127.8, 127.6, 127.0, 126.0, 118.1, 107.9. HRMS (EI): Calcd for $C_{19}H_{13}NS$: 287.0769. Found: 287.0762.

(Z)*-2-(Biphenyl-4-yl)-3- (furan-2-yl)acrylonitrile* (**2b**): Yellow solid Yield: 95%. M.p. 171 °C. FTIR (KBr pellet, cm^{-1}): 3125, 3023, 2215, 1610, 1588, 1487, 1463, 1403, 1330, 1083, 1025, 929, 885, 838, 764, 721, 691, 585, 475. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.73 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.63 (d,J = 7.2 Hz, 3H), 7.47 (m, 3H), 7.39 (dd, J = 7.2 Hz, J = 7.2 Hz, 1H), 7.24 (d, J = 3.6 Hz, 1H), 6.60 (dd, J = 1.6 Hz, J = 2.0Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 150.0, 144.6, 141.6, 139.6, 132.3, 128.6, 127.5, 127.4, 127.3, 126.7, 125.7, 117.4, 115.0, 112.6, 107.0. HRMS (EI): Calcd for $C_{13}H_8NO$: 271.0997. Found: 271.0998.

(Z)*-2-(4-Methylbiphenyl-4-yl)-3-(thiophen-2-yl)acrylonitrile* (**2c**): Yellow solid. Yield: 90%. M.p. 186 °C. FTIR (KBr pellet, cm^{-1}): 3089, 2209, 1604, 1583, 1493, 1417, 1205, 1053, 809, 718. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.70 (d, J = 6.8 Hz, 2H), 7.68 (d, J = 6.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 4.8 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 2.0 Hz, 2H), 7.16 (dd, J = 4.4 Hz, J = 4.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 141.7, 138.0, 137.7, 137.0, 133.6, 132.4, 132.3, 129.9, 129.6, 127.8, 127.4, 126.8, 126.0, 118.1, 107.9, 21.1. HRMS (EI): Calcd for $C_{20}H_{15}NS$: 301.0925. Found: 301.0934.

(Z)*-2-(4-Methylbiphenyl-4-yl)-3-(furan-2-yl)acrylonitrile* (**2d**): Yellow solid. Yield: 94%. M.p. 182 °C. FTIR (KBr pellet, cm^{-1}): 3141, 3017, 2949, 2362, 2213, 1612, 1498, 1466, 1398, 1329, 1026, 887, 809, 746, 586, 475. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.71 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 1.2Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.43 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 3.6 Hz, 1H), 6.60 (dd, J = 1.6 Hz, J = 2.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 150.0, 144.6, 141.5, 137.5, 136.7, 132.0, 129.4, 127.2, 126.5, 125.7, 117.5, 114.9, 112.6, 107.1, 20.9. HRMS (EI): Calcd for $C_{20}H_{15}NO$: 285.1154. Found: 285.1155.

(Z)*-2-(4-Methoxybiphenyl-4-yl)-3-(thiophen-2-yl)acrylonitrile* (**2e**): Yellow solid. Yield: 91 %. M.p. 178 °C. FTIR (KBr pellet, cm^{-1}): 3069, 2980, 2970, 2209, 1600, 1586, 1492, 1417, 1210, 1205, 1051, 801, 713. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.71 (d, J = 4.8 Hz, 2H), 7.69 (d, J = 3.2 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.59 (s, 1H), 7.50 (d, J = 5.2 Hz, 2H), 7.18 (dd, J = 3.6 Hz, J=3.2 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_c: 160.1, 140.2, 138.0, 137.6, 135.8, 134.2, 133.5, 132.8, 132.4, 130.1, 128.3, 127.9, 118.3, 114.4, 107.2, 55.3. HRMS (EI): Calcd for $C_{20}H_{16}NOS$: 317.0874. Found: 317.0875.

(Z)-*2-(4-Methoxybiphenyl-4-yl)-3-(furan-2-yl)acrylonitrile* (**2f**): Yellow solid. Yield: 94%. M.p. 150 °C. FTIR (KBr pellet, cm^{-1}): 3125, 3034, 2940, 2215, 1611, 1588, 1464, 1402, 1330, 1087, 1026, 1003, 932, 886, 839, 764, 722, 692, 589, 474. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.69 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.2 Hz, 3H), 7.57 (d, J = 8.4 Hz, 2H), 7.42 (s, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.60 (dd, J = 1.2 Hz, J = 1.6 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_c: 159.6, 150.2, 144.8, 141.4, 132.4, 131.9, 128.0, 127.3, 127.1,125.9, 117.7, 115.0, 114.3, 112.8, 107.2, 55.3. HRMS (EI): Calcd for $C_{20}H_{15}NO_2$: 301.1103. Found: 301.1105.

(Z)-*2-(3,5-Dimethylbiphenyl-4-yl)-3-(thiophen-2-yl)acrylonitrile* (**2g**): Yellow solid. Yield: 87 %. M.p. 103 °C. FTIR (KBr pellet, cm^{-1}): 3088, 3049, 2914, 2210, 1602, 1585, 1417, 1401, 1384, 1204, 1054, 832, 808, 717, 702. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.69 (d, J = 7.6 Hz, 3H), 7.63 (d, J = 8.0 Hz, 2H),7.55 (d, J = 5.2 Hz, 1H), 7.24 (d, J = 8.8 Hz, 3H), 7.16 (dd, J = 4.4 Hz, J = 4.8 Hz, 1H), 7.03 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_c:141.2, 141.0, 138.5, 137.6, 135.8, 134.2, 132.2, 130.0, 129.9, 128.8, 127.7, 125.8, 125.2, 118.2, 105.2, 21.3. HRMS (EI): Calcd for $C_{21}H_{17}NS$: 315.1082. Found: 315.1085.

(Z)-*2-(3,5-Dimethylbiphenyl-4-yl)-3-(furan-2-yl)acrylonitrile* (**2h**): Yellow solid. Yield: 92%. M.p. 62 °C. FTIR (KBr pellet, cm^{-1}): 3141, 3023, 2914, 2366, 2214, 1617, 1605, 1501, 1469, 1331, 1032, 1022, 886, 827, 763, 695, 580. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.67 (d, J = 8.0 Hz, 2H), 7.60 (dd, J = 8.0 Hz, J = 6.0 Hz, 3H), 7.40 (s, 1H), 7.21 (s ,3H), 7.01 (s, 1H), 6.57 (dd, J = 1.6Hz, J = 2.0 Hz, 1H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_c: 150.2, 144.9, 142.1, 139.9, 138.5, 132.3, 129.5, 127.7, 127.5, 125.8, 124.9, 117.8, 115.2, 112.9, 107.3, 21.4. HRMS (EI): Calcd for $C_{21}H_{17}NO$: 299.131. Found: 299.137.

(Z)-*2-[4-(2-Naphthyl)phenyl]-3-(thiophen-2-yl)acrylonitrile* (**2i**): Yellow solid. Yield: 82%. M.p. 70 °C. FTIR (KBr pellet, cm^{-1}): 3111, 3025, 2209, 1578, 1485, 1421, 1361, 1211, 1054, 839, 765,719. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 7.93 (dd, J = 8.0 Hz, J = 7.6 Hz, 3H), 7.79 (d, J = 7.6 Hz, 3H), 7.72 (d, J = 3.6 Hz, 1H), 7.60–7.45 (m, 7H), 7.19(dd, J = 4.0 Hz, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_c: 141.5, 139.1, 138.0, 134.2, 133.9, 132.8, 132.7, 131.4, 130.8, 130.2, 128.5, 128.2, 127.0, 127.0, 126.4, 126.0, 125.7, 125.6, 125.5, 118.3, 107.9. HRMS (EI): Calcd for $C_{23}H_{15}NS$: 337.0925. Found: 337.0928.

(Z)-*3-(Furan-2-yl)-2-[4-(2-naphthyl)phenyl]acrylonitrile* (**2j**): Yellow solid. Yield: 89%. M.p. 145 °C. FTIR (KBr pellet, cm^{-1}): 3127, 3053, 2214, 1596, 1501, 1466, 1333, 1246, 1131, 1019, 884, 819, 753, 589, 487. ^{1}H NMR (400, MHz CDCl$_3$) δ_H: 8.09 (s, 1H), 7.94 (dd, J = 8.4 Hz, J = 8.0 Hz, 2H), 7.89 (d, J = 6.8 Hz, 1H), 7.82–7.58 (m, 5H), 7.64 (d, J = 1.2 Hz, 1H), 7.55–7.52 (m, 2H), 7.47 (s, 1H), 7.26 (d, J = 3.6 Hz, 1H), 6.62 (dd, J = 1.6 Hz, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ_c: 150.2, 144.9, 141.6, 137.1, 133.6, 132.8, 132.6, 128.6, 128.2, 127.9, 127.6, 127.6, 126.5, 126.2, 126.0, 125.8, 125.1, 117.7, 115.3, 112.9, 107.2. HRMS (EI): Calcd for $C_{23}H_{15}NO$ 321.1154. Found: 321.1158.

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