Synthesis and photophysical properties of novel fluorescent quinoline-based aryl substituted styryl systems

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Synthesis of (*E*)-2-(4-bromostyryl)quinoline has been easily achieved by an acid catalysed condensation of 2-methylquinoline with 4-bromobenzaldehyde. Various boronic acid derivatives reacted with (*E*)-2-(4-bromostyryl)quinoline to afford a series of novel quinoline-based aryl substituted styryl derivatives by the catalysis of $Pd(PPh_3)_4$ at 85 °C in dimethoxyethane. The UV-Vis absorption and photoluminescent spectra of them in CH_2Cl_2 were investigated.

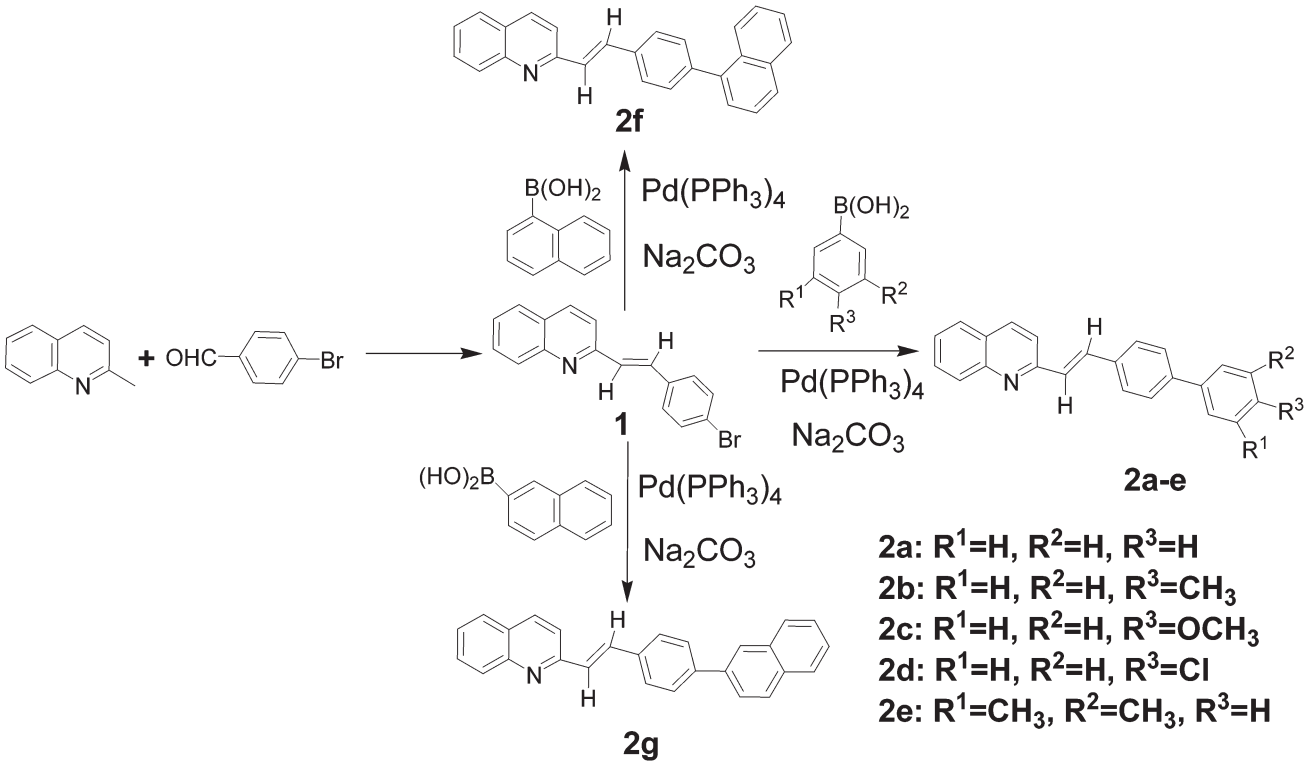
Keywords: quinoline, styryl systems, biaryl units, aryl bromide, Pd-catalysed

The emerging field of organic light-emitting diodes (OLEDs)[1] is attracting considerable interest owing their technological promise for the development of next generation low cost full-colour displays and emissive products.[2–4] Among OLED materials, the use of organic conjugated materials as active elements in light-emitting displays, envisioned nearly two decades ago, has now reached the stage of commercialisation.[5] For material research, quinoline as fluorescent compounds of high quantum yield is an electron-deficient system with good thermal stability, comparatively easy to prepare and has excellent electroluminescent properties when the quinoline is suitability substituted at the right positions.[6,7] Biaryl units and quinoline ring system[8] as versatile intermediates in organic synthesis and essential structural fragment of a large number of natural and unnatural compounds possessing a wide range of pharmacological and biological activity,[9,10] in addition to their application in materials science.

We have previously shown the preparation of a series of novel, functionalised arylamine and acrylonitrile[4,11–14] derivatives as promising compounds for application in electronic devices. We now report the design and synthesis of several novel fluorescent quinoline-based aryl substituted styryl derivatives via palladium-catalysed coupling.

The target compounds (**2a–g**) were obtained by a two-step procedure. (see Scheme 1). The synthesis of (*E*)-2-(4-bromostyryl)quinoline has been reported in our previous work.[15] It was an acid catalysed condensation of 2-methylquinoline and 4-bromobenzaldehyde. For the second step, various boronic acid derivatives reacted with the (*E*)-2-(4-bromostyryl) quinoline to afford quinoline-based aryl substituted styryl compounds by the catalysis of $Pd(PPh_3)_4$ at 85 °C in dimethoxyethane. The *E/Z* isomerisation proportions of target compounds are between 98/2 and 91/9. This reaction may be a photoreversible process.[16] The yields, isomerisation proportions of the products as well as the reaction time were shown in Table 1.

In order to investigate the photophysical properties of the quinoline-based aryl substituted styryl derivatives, the UV and PL spectra (Table 2) in dilute dichloromethane solution were recorded. Most of them displayed two absorption peaks in



Scheme 1

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Table 1 Structures, reaction conditions and yields of novel compounds

Entry	R^1	R^2	R^3	Time/h	*E*/*Z*	Yields/%
2a	H	H	H	5	95/5	90
2b	H	H	CH_3	8	95/5	85
2c	H	H	OCH_3	5	93/7	87
2d	H	H	Cl	6	91/9	80
2e	CH_3	CH_3	H	5	96/4	83
2f	—	—	—	5	93/7	77
2g	—	—	—	7	98/2	84

Table 2 Photophysical properties of compounds **2a–g**

Entry	$^a\lambda_{max}{}^{abs}$/nm	$^b\lambda_{max}{}^{em}$/nm
2a	306, 361	409
2b	302, 355	418
2c	304, 370	442
2d	307, 358	405
2e	304, 357	414
2f	293, 356	430
2g	295, 368	423

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

the UV spectra at about 293–307 nm which were ascribed to the absorption in a π–π* transition of the compounds and 355–370 nm assigned to the absorbing transition of intermolecular electron transfer. As Table 2 shows, when R^3 was electron donating group (methoxy) (**2c**), the absorption maximum was redshifted by 12 nm compared to when R^3 was electron-withdrawing group (chlorine) (**2d**), which showed that there was obvious electron transfer with the change of the substituent group in conjugated system.

The emission peaks of compounds were located at about 405–442 nm. The emission peak of **2c** was redshifted by 37 nm compared to the compound of **2d**. All compounds yield blue emissions in CH_2Cl_2 solution at room temperature.

Conclusion

In conclusion, several novel quinoline-based aryl substituted styryl derivatives have been synthesised. This methodology requires mild conditions and employs very simple starting materials and inexpensive and easily handled catalysts. The absorption and photoluminescent spectra of these derivatives 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 405–442 nm.

Experimental

The boronic acid derivatives, tetrakis(triphenylphosphine)palladium were products of the Aldrich Chemical Co. Sodium carbonate 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. All melting points were determined with a WRS-1A melting point apparatus and were uncorrected. NMR (^{1}H NMR and ^{13}C NMR) spectra were run on a Bruker AV-400 NMR spectrometer in $CDCl_3$ and chemical shifts 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 HP5989B mass spectrometer. Elemental analysis was performed on 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.

(*E*)-*2-(4-bromostyryl)quinoline* (**1**):[15] A solution of 2-methyquinoline 10.5 g (0.0734 mol), 4-bromobenzaldehyde (0.084 mol) and 5 g (0.0375 mol) of acetic anhydride was heated at 150 °C for 16 h in a 50 mL round bottomed flask fitted with a reflux condenser. The hot solution was poured into 10% sodium hydroxide solution (50 mL). After the oil congealed, the solid was removed by filtration, washed with water and then with ice cold ethanol (10 mL) and dried at 60 °C. 60–70% yield. White solid, yield: 68%. M.p. 133–134 °C. (lit.[15] 133–134 °C), FTIR (KEr pellet, cm^{-1}): 3045, 1588, 1498, 1395, 1062, 1005, 965, 821, 745. ^{1}H NMR(400 MHz, $CDCl_3$) δ_H: 8.11 (d, *J* = 8.8 Hz,1 H), 8.07 (d, *J* = 8.4, 1 H), 7.77 (d, *J* = 8.8 Hz, 1 H), 7.70 (dd, *J* = 7.6 Hz, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 3.6 Hz, 1 H), 7.60 (d, *J* = 4.0 Hz 1 H); 7.50 (m, 5 H), 7.37 (d, *J* = 16 Hz 1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 155.5, 148.2, 136.5, 135.5, 133.1, 131.9, 129.9, 129.6, 129.2, 128.7, 127.5, 127.4, 126.3, 122.5, 119.3.

Synthesis of novel conjugated quinoline derivatives; general procedure

To a 25 mL sidearm flask was added compound **1** (1.00 mmol), boronic acid derivatives (1.10 mmol), $Pd(PPh_3)_4$ (0.012 mmol) and sodium carbonate (0.233 g, 2.20 mmol). Water (2.0 mL), EtOH (3.0 mL), dimethoxyethane (7.5 mL) was injected into the flask from a syringe. The reaction mixture was heated and stirred at 85 °C under nitrogen for an appropriate time until the reaction was 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 $MgS0_4$. Concentration of the filtrate on a rotary evaporator followed by washing of the solid material with ice cold ethanol afforded the desired crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:10) as eluents.

(*E*)-*2-[2-([1,1′-biphenyl]-4-yl)vinyl]quinoline* (**2a**):[17] Pale yellow solid, yield: 90%. M.p. 192–193 °C [lit.[17] 186 °C(C_6H_6)]. FT-IR (KBr pellet, cm^{-1}): 3017, 2363, 1655, 1637, 1558, 1510, 1384, 830, 765, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.12(d, *J* = 8.8 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 7.78(d, *J* = 8.4 Hz,1 H), 7.74–7.67 (m, 5 H), 7.65–7.62 (m, 4 H), 7.50 (d, *J* = 7.6 Hz, 1 H). 7.47–7.43 (m, 3 H), 7.35 (dd, *J* = 7.6 Hz , *J* = 6.8 Hz ,1 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 157.00, 148.17, 141.34, 140.46, 136.41, 135.47, 134.06, 130.86, 129.67, 129.52, 129.15, 128.83, 127.73, 127.51, 126.91, 126.44, 126.20, 122.23, 119.29. MS *m/z*: 307 (M^+).

(*E*)-*2-[2-(4′-methyl-[1,1′-biphenyl]-4-yl)vinyl]quinoline* (**2b**): Pale yellow solid, yield: 85%. M.p. 226–227 °C. FT-IR (KBr pellet, cm^{-1}): 3019, 2917, 2360, 1648, 1623, 1558, 1507, 1384, 872, 824. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.16–8.10 (m, 2 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.76–7.69 (m, 5 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.54–7.44 (m, 2 H), 7.29–7.24 (m, 2 H), 2.42 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 155.99, 148.18, 141.28, 140.51, 137.35, 136.35, 135.21, 134.06, 130.72, 129.51, 129.15, 128.72, 127.69, 127.48, 127.21, 126.64, 126.15, 122.24, 119.27, 21.11. MS *m/z*: 321 (M^+). Anal. Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.37; H, 5.87; N, 4.32%.

(*E*)-*2-[2-(4′-methoxy-[1,1′-biphenyl]-4-yl)vinyl]quinoline* (**2c**): Pale yellow solid, yield: 87%. M.p. 209–210 °C. FT-IR (KBr pellet, cm^{-1}): 3017, 2913, 2360, 1654, 1625, 1558, 1507, 1384, 872, 824. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.16 (d, *J* = 8.8 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.76–7.71 (m, 5 H), 7.61 (dd, *J* = 9.2 Hz, *J* = 8.4 Hz, 4 H), 7.56–7.44 (m, 2 H), 7.02–6.97 (m, 2 H). 3.88 (s,3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 156.02, 148.18, 140.96, 140.18, 136.36, 134.87, 134.10, 132.96, 130.62, 129.65, 129.10, 128.55, 127.98, 127.72, 127.48, 126.93, 126.37, 119.26, 114.27, 55.17. MS *m/z*: 337 (M^+). Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.25; H, 5.59; N, 4.08%.

(*E*)-*2-[2-(4′-chloro-[1,1′-biphenyl]-4-yl)vinyl]quinoline* (**2d**): Pale yellow solid, yield: 80%. M.p. 190–191 °C. FT-IR (KBr pellet, cm^{-1}): 3023, 2360, 1657, 1631, 1558, 1507, 1384, 827, 758. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.15 (d, *J* = 8.0 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.76–7.69 (m, 5 H), 7.63–7.49 (m, 5 H), 7.45–7.40 (m, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 155.83, 148.24, 139.92, 138.87, 136.36, 135.85, 133.71, 130.91, 129.79, 129.18, 128.98, 128.14, 127.79, 127.51, 127.24, 126.68, 126.22, 122.18, 119.31. MS *m/z*: 341 (M^+). Anal. Calcd for $C_{23}H_{16}ClN$: C, 80.81; H, 4.72; N, 4.10. Found: C, 80.31; H, 4.68; N, 3.95%.

(*E*)-*2-[2-(3′,5′-dimethyl-[1,1′-biphenyl]-4-yl)vinyl]quinoline* (**2e**): Pale yellow solid, yield: 83%. M.p. 142–143 °C. FT-IR (KBr pellet, cm^{-1}): 3017, 2913, 2360, 1637, 1597, 1560, 1501, 1384, 830, 752. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.11 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.74–7.67 (m, 5 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.52–7.43 (m, 2 H), 7.26 (s, 2 H), 7.02 (1 H), 2.40 (s, 6 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 156.01, 148.22, 141.59, 140.46, 138.33, 136.35, 135.32, 134.07, 129.77, 129.18, 129.14, 128.76,

127.63, 127.51, 127.47, 127.31, 126.16, 124.89, 119.25, 21.42. MS *m/z*: 335 (M^+). Anal. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.29; H, 6.18; N, 4.03%.

(*E*)-*2-[4-*(*naphthalen-1-yl*)*styryl]quinoline* (**2f**): Pale yellow solid, yield: 77%. M.p. 148–149 °C. FT-IR (KBr pellet, cm^{-1}): 3028, 2359, 1637, 1598, 1560, 1508, 1384, 869, 824, 776. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27(d, *J* = 8.8 Hz, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.8 Hz,1 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.85–7.75 (m, 5 H), 7.64–7.61 (m, 1 H), 7.59–7.49 (m, 8 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 156.01, 148.27, 141.21, 139.74, 136.50, 135.55, 134.2, 133.99, 133.19, 131.98, 131.55, 130.65, 129.95, 129.54, 129.17, 128.75, 128.52, 128.00, 127.70, 127.35, 127.09, 126.20, 126.00, 125.56, 119.39. MS *m/z*: 357 (M^+). Anal. Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.92. Found: C, 90.38; H, 5.23; N, 4.10%.

(*E*)-*2-[4-*(*naphthalen-2-yl*)*styryl]quinoline* (**2g**): Pale yellow solid, yield: 84%. M.p. 216–217 °C. FT-IR (KBr pellet, cm^{-1}): 3031, 2360, 1637, 1597, 1560, 1508, 1384, 869, 826, 778. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.15–8.09 (m, 3 H),7.92 (dd, *J* = 8.8 Hz, *J* = 7.2 Hz,2 H), 7.87 (d, *J* = 7.24 Hz, 1 H), 7.80–7.77(m, 6 H), 7.74–7.69 (m, 3 H), 7.51–7.47 (m, 4 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ_c: 155.90, 148.16, 141.24, 137.78, 136.43, 135.60, 134.07, 133.67, 132.73, 130.38, 129.51, 128.49, 128.22, 127.81, 127.68, 127.48, 127.34, 127.11, 126.33, 126.20, 126.03, 125.68, 125.23, 122.22, 119.28. MS *m/z*: 357 (M^+). Anal. Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.92. Found: C, 90.41; H, 5.19; N, 3.77%.

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