

Synthesis and photophysical properties of conjugated quinolines

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Aryl halides were prepared by condensation of 2-methylquinoline and bromo- or chloro-arylaldehydes in acetic anhydride. Diarylamines reacted with the aryl halides to afford novel triarylamine derivatives using $\text{Pd}(\text{OAc})_2/\text{P}(o\text{-tolyl})_3$ as catalyst. These compounds have potential as organic light-emitting device materials and were characterised by FT-IR, ^1H NMR and elemental analyses. The UV-vis absorption and photoluminescent spectra of the compounds in CH_2Cl_2 were investigated. The lowest absorption band of the triarylamine derivatives centred at about 400 nm was assigned to a charge-transfer transition with an emission at 500–515 nm.

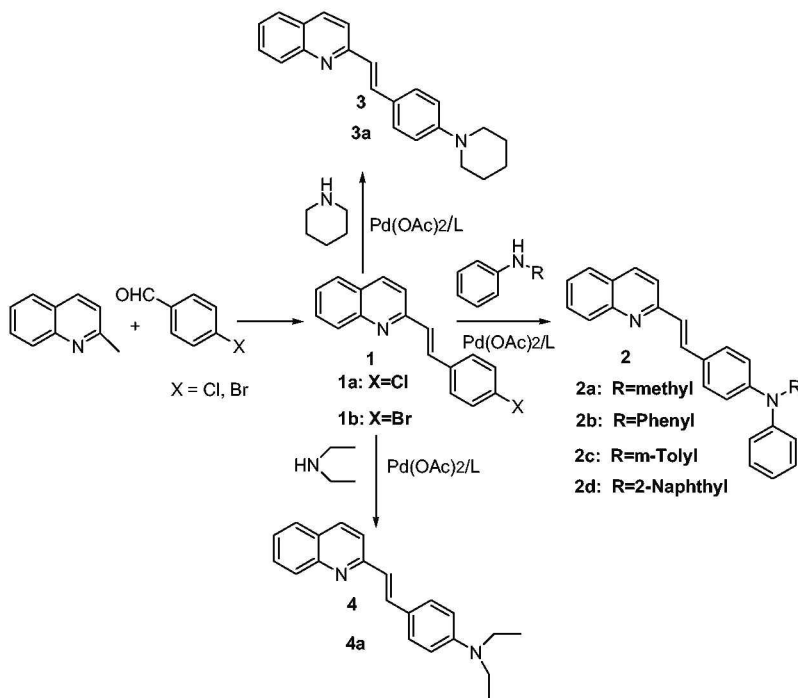
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Considerable studies have been made on organic light-emitting diodes (OLEDs) for their potential applications in next generation full-colour displays as a promising alternative to the conventional liquid crystal displays.^{1,2} Among OLED materials, triarylamine derivatives have been widely investigated for almost two decades because these compounds have showed excellent thermal and electrochemical stability, electron-donating ability, optoelectronic properties,^{3–5} and they are standard hole transport materials.^{6–8} Several carbazole derivatives and diaminoanthracene derivatives are very efficient both as hole transporters and green emitters.^{9,10} There has been a considerable effort in synthetic chemistry and most triarylamine derivatives are obtained through palladium-catalysed cross-coupling reactions involving formation of a C–N single bond.

Novel green compounds combining both hole-transporting triarylamines and electron-transporting quinoline groups have attracted great attention. We chose triarylamines as the building blocks due to their high hole-transporting mobility.^{11–13}

Based on our long standing studies in the field of organic light-emitting devices^{9,14} as well as in palladium-catalysed coupling reactions, we have designed and synthesised a series of triarylamine derivatives with quinoline groups and their UV-visible spectra (UV) and photoluminescence (PL) properties have been studied. The reaction steps are outlined in Scheme 1.

The target compounds were obtained by a two-step procedure. Aryl bromides or chlorides containing a quinoline group were prepared by the reaction of 2-methylquinoline and 4-bromobenzaldehyde or 4-chlorobenzaldehyde in acetic anhydride at 150 °C for 16 h. The yields were in the 60–70% range. For the second step, diarylamines reacted with the aryl bromides or chlorides to afford triarylamine derivatives in the presence of the catalyst $\text{Pd}(\text{OAc})_2/\text{P}(o\text{-tolyl})_3$. Standard conditions were 1.2 mmol aryl bromide or chloride, 1.0 mmol amine, 1.5 mmol sodium *tert*-butoxide, 0.05 mmol palladium(II), and 0.15 mmol $\text{P}(o\text{-tolyl})_3$ in toluene at 110 °C for 8–24 h.



Scheme 1

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Table 1 Physical properties of triarylamines

Entry	$\lambda_{\max}^{\text{absa}}/\text{nm}$	$\lambda_{\max}^{\text{emb}}/\text{nm}$
2a	294, 392	500
2b	307, 403	504
2c	308, 406	513
2d	321, 409	516
3a	379	511
4a	295, 401	506

^aMaximum absorption wavelength in CH_2Cl_2 .

^bMaximum emission wavelength in CH_2Cl_2 .

In order to investigate the photophysical properties of the triarylamines derivatives, the UV and PL spectra (Table 1) in dilute dichloromethane solution were recorded. All compounds yield green emissions in solution at room temperature.

As indicated in the absorption spectra Fig. 1, the absorption behaviours were quite similar to each other, and most of them displayed two absorption peaks at about 300 nm and 400 nm (except 3a) which were ascribed to the absorption by the triarylamines moiety in a $\pi-\pi^*$ transition. As Table 1 shows, when R is 2-naphthyl (2d), the absorption maximum was redshifted by 17 nm compared to when R is methyl (2a), which showed that there was obvious $\pi-\pi^*$ delocalisation with the increase in benzene rings present.

Figure 2 outlines the emission spectra of the compounds in CH_2Cl_2 . The emission peaks of compounds are located at about 500 nm in the green region. When R is 2-naphthyl (2d), the emission peak was redshifted by 16 nm compared to the compound of 2a.

Conclusion

In conclusion, several novel triphenylamine derivatives have been synthesised. The absorption and photoluminescent spectra of these derivatives in CH_2Cl_2 were investigated. These compounds exhibit similar absorption and emission behaviours and emit strongly in solution, with the emission maxima in the range of 500–515 nm.

Experimental

The aromatic amines, palladium(II) and tri-*o*-tolylphosphine were products of the 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. All melting points were determined with a WRS-1A melting point apparatus and were uncorrected. Proton NMR (^1H 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 an internal standard. IR spectra were recorded in KBr on a Nicolet NEXUS 470 FT-IR

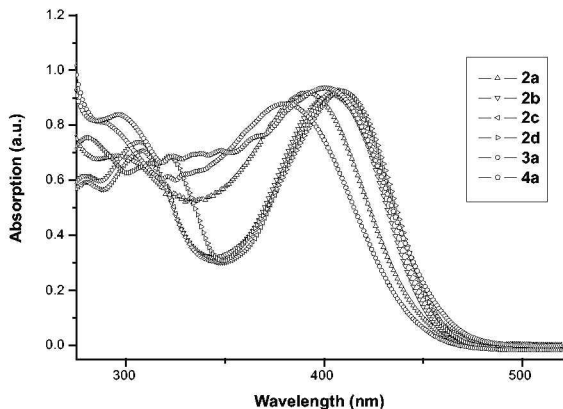


Fig. 1 Absorption spectra of novel compounds in CH_2Cl_2 .

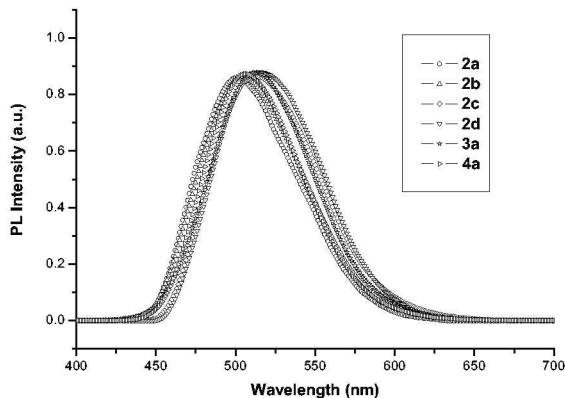


Fig. 2 Photoluminescence spectra of novel compounds in CH_2Cl_2 .

spectrophotometer. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). 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.

General procedure for the synthesis of the aryl bromides or chlorides containing quinoline groups

A solution of 2-methylquinoline 10.5 g (0.0734 mol), 4-bromo- or 4-chloro-benzaldehyde (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.

(E)-2-(4-chlorostyryl)quinoline (1a): White solid, Yield: 65%. M.p. 143°C . FTIR (KBr pellet, cm^{-1}): 3045, 1588, 1498, 1395, 1095, 974, 824, 737. ^1H NMR (400, CDCl_3) δ_{H} : 8.11 (d, $J = 8.4$ Hz, 1 H), 8.08 (d, $J = 8.4$, 1 H), 7.77 (d, $J = 8.4$ Hz, 1 H), 7.71 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1 H), 7.64 (d, $J = 10.4$ Hz, 1 H), 7.61 (d, $J = 2.4$ Hz, 1 H); 7.55 (s, 1 H), 7.53 (s, 1 H), 7.50 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 1 H), 7.35 (m, 3 H). ^{13}C NMR (400 MHz, CDCl_3) δ_{C} : 155.5, 148.2, 136.4, 135.0, 134.3, 133.0, 129.8, 129.5, 129.2, 129.0, 128.4, 127.5, 127.4, 126.3, 119.3. Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{ClN}$: C, 76.84; H, 4.55; N, 5.27. Found: C, 76.81; H, 4.59; N, 5.21%.

(E)-2-(4-bromostyryl)quinoline (1b): White solid, Yield: 68%. M.p. $133-134^\circ\text{C}$. FTIR (KBr pellet, cm^{-1}): 3045, 1588, 1498, 1395, 1062, 1005, 965, 821, 745. ^1H NMR (400, 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. Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{BrN}$: C, 65.83; H, 3.90; N, 4.52. Found: C, 65.84; H, 3.98; N, 4.57%.

General procedure for the synthesis of conjugated quinolines

To a 25 mL sidearm flask was added the aryl bromide or chloride containing a quinoline group (1.20 mmol), aromatic amine (1.00 mmol), $\text{Pd}(\text{OAc})_2$ (0.06 mmol, Pd/Br = 5%), $\text{P}(o\text{-tolyl})_3$ (0.18 mmol) and sodium *tert*-butoxide (1.50 mmol). Toluene (10 mL) was injected into the flask from a syringe. 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 ethyl acetate/hexane (1 : 10) as eluent.

(E)-N-methyl-N-(4-(2-(quinolin-2-yl)vinyl)phenyl)benzenamine (2a): Yellow solid, Yield: 60%. M.p. $121-123^\circ\text{C}$. FTIR (KBr pellet, cm^{-1}): 3057, 2926, 1588, 1552, 1514, 1494, 1346, 1182, 1117, 826, 752, 697. ^1H NMR (400, CDCl_3) δ_{H} : 8.12 (d, $J = 8.4$ Hz, 1 H), 8.05 (d, $J = 8.8$, 1 H), 7.64–7.74 (m, 4 H), 7.63 (d, $J = 8.4$ Hz, 2 H), 7.47 (dd, $J = 6.8$ Hz, $J = 7.6$ Hz, 1 H), 7.30–7.40 (m, 3 H), 7.13–7.21

(m, 3H), 6.96 (d, $J = 8.0$ Hz, 2H), 3.36 (s, 3H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.5, 148.6, 148.4, 147.5, 136.3, 134.3, 130.1, 129.7, 129.0, 127.9, 127.8, 127.3, 127.1, 126.8, 124.7, 119.2, 119.1, 118.7, 118.3, 41.5. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.66; H, 5.92; N, 8.28%.

(E)-N-phenyl-N-(4-(2-(quinolin-2-yl)vinyl)phenyl)benzenamine (**2b**): Yellow solid, Yield: 58%. M.p. 150–151 °C. FTIR (KBr pellet, cm^{-1}): 3034, 2925, 1588, 1508, 1490, 1330, 1282, 1315, 1176, 832, 750, 695. ^1H NMR (400, CDCl_3) δ_{H} : 8.09 (d, $J = 8.4$ Hz, 2 H), 7.77 (d, $J = 8.0$, 1 H), 7.70 (dd, $J = 7.6$ Hz, $J = 7.2$ Hz, 1 H), 7.66 (s, 1 H), 7.63 (d, $J = 8.0$ Hz, 1 H), 7.53 (s, 1 H); 7.50 (t, $J = 8.4$ Hz, $J = 7.2$ Hz, 2 H), 7.30 (m, 5 H), 7.16 (d, $J = 8.0$ Hz, 4 H), 7.08 (dd, $J = 8.0$ Hz, $J = 7.2$ Hz, 4H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.4, 148.4, 148.3, 147.3, 136.2, 134.0, 130.2, 129.7, 129.4, 129.0, 128.2, 127.5, 127.2, 127.0, 125.9, 124.9, 123.4, 122.8, 119.1. Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.32; H, 5.54; N, 7.03%.

(E)-3-methyl-N-phenyl-N-(4-(2-(quinolin-2-yl)vinyl)phenyl)benzenamine (**2c**): Yellow solid, Yield: 55%. M.p. 149–150 °C. FTIR (KBr pellet, cm^{-1}): 3032, 2925, 1588, 1508, 1489, 1314, 1280, 1180, 691, 832, 753, 701. ^1H NMR (400, CDCl_3) δ_{H} : 8.09 (d, $J = 8.4$ Hz, 2 H), 7.76 (d, $J = 8.0$, 1 H), 7.70 (dd, $J = 7.6$ Hz, $J = 8.0$ Hz, 1 H), 7.66 (s, 1 H), 7.63 (d, $J = 8.8$ Hz, 2 H), 7.50 (m, 3 H); 7.30 (m, 3 H), 7.17 (m, 3 H), 7.08 (m, 3 H), 6.95 (m, 3 H), 2.3 (s, 3 H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.5, 148.6, 148.3, 147.4, 147.3, 139.3, 136.2, 134.1, 130.0, 129.7, 129.3, 129.2, 129.0, 128.2, 127.5, 127.2, 126.9, 125.9, 125.8, 124.9, 124.5, 123.3, 122.7, 122.3, 119.1, 21.4. Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2$: C, 87.35; H, 5.86; N, 6.79. Found: C, 87.40; H, 5.78; N, 6.86%.

(E)-N-phenyl-N-(4-(2-(quinolin-2-yl)vinyl)phenyl)naphthalene-2-amine (**2d**): Yellow solid, Yield: 50%. M.p. 168–169 °C. FTIR (KBr pellet, cm^{-1}): 3056, 2927, 1591, 1506, 1491, 1315, 1294, 1279, 1179, 817, 747, 695. ^1H NMR (400, CDCl_3) δ_{H} : 8.10 (t, $J = 8.4$ Hz, $J = 12.0$ Hz, 2 H), 7.77 (m, 3 H), 7.67 (m, 4 H), 7.52 (m, 4 H), 7.40 (m, 2 H), 7.33 (m, 4 H); 7.19 (d, $J = 7.6$ Hz, 2 H), 7.12 (m, 3 H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.3, 148.3, 147.3, 144.9, 136.2, 134.4, 134.0, 134.0, 130.6, 130.4, 129.7, 129.4, 129.1, 128.3, 127.6, 127.5, 127.2, 127.2, 127.1, 127.0, 126.4, 126.0, 125.1, 124.8, 124.7, 123.6, 123.1, 121.3, 119.1. Anal. Calcd for $\text{C}_{33}\text{H}_{24}\text{N}_2$: C, 88.36; H, 5.39; N, 6.25. Found: C, 88.43; H, 5.37; N, 6.20%.

(E)-2-(4-(piperidin-1-yl)styryl)quinoline (**3a**): Yellow solid, Yield: 57%. M.p. 110–111 °C. FTIR (KBr pellet, cm^{-1}): 3031, 2927, 1594, 1515, 1451, 1426, 1236, 1187, 1128, 825, 753. ^1H NMR (400, CDCl_3) δ_{H} : 8.06 (t, $J = 8.8$ Hz, $J = 7.6$ Hz, 2 H), 7.69 (m, 3 H), 7.54 (m, 2 H), 7.23 (m, 3 H), 6.92 (d, $J = 8.8$ Hz, 2 H), 3.25 (t, $J = 5.2$ Hz, $J = 6.0$ Hz, 4 H); 1.70 (m, 4 H), 1.61 (m, 2 H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.5, 148.5, 148.2, 136.3, 134.1, 129.4, 129.0, 128.2,

127.5, 127.2, 126.9, 125.9, 124.9, 119.1, 114.9, 52.0, 25.9, 25.6. Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.39; H, 7.09; N, 8.86%.

(E)-N,N-diethyl-4-(2-((4-(quinolin-2-yl)vinyl)benzenamine (**4a**): Yellow solid, Yield 58%. M.p. 101–103 °C. FTIR (KBr pellet, cm^{-1}): 3030, 2973, 2919, 1588, 1519, 1089, 1050, 825, 750, 668. ^1H NMR (400, CDCl_3) δ_{H} : 8.05 (t, $J = 8.4$ Hz, $J = 9.6$ Hz, 2 H), 7.69 (m, 3 H), 7.54 (m, 2 H), 7.23 (m, 3 H), 6.69 (d, $J = 8.8$ Hz, 2 H), 3.40 (m, 4 H); 1.20 (m, 6 H). ^{13}C NMR (400 MHz, CDCl_3): δ_{c} : 156.5, 148.4, 148.2, 136.3, 134.1, 129.3, 129.1, 128.2, 127.5, 127.2, 126.8, 126.0, 124.8, 119.1, 114.8, 44.8, 13.2. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.32; H, 7.39; N, 9.21%.

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