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The synthesis and photophysical properties of novel poly(diarylamino)styrenes

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ABSTRACT

A series of novel diamines linked by varying conjugated bridges were characterized using FTIR, NMR and UV–visible spectroscopy, mass spectrometry and elemental analysis. The photoluminescence and thermal properties of the compounds were related to structure and quantum chemical calculations were employed to study the optimized ground state geometry of the compounds. The diarylamines exhibited blue to green fluorescence emission and displayed high thermal stability and high glass transition temperature. As such, the compounds might be very useful as hole-transporting materials in organic light-emitting diodes.

1. Introduction

Organic fluorescent compounds have been extensively investigated for a myriad of potential applications including as biological labels, in photovoltaic cells, in light-emitting diodes (LEDs), and as optical sensors etc [1–17]. Fluorescent characteristics rely largely on molecular structure and molecular assembly. Although there have been some reports on structure–property relationship of fluorescence [15–17], a clear understanding has not been fully revealed so far. Therefore, it is significant to explain the structure–property relationship of fluorescence because such a relationship would enable the design of more useful fluorescent reagents and probes which might be applied in the fields of analytical and biological chemistry in the future.

Arylamine-based derivatives are well-known electron-rich compounds which are widely employed as hole-transporting materials, and light emitters in the field of optoelectronics such as organic light-emitting diodes (OLEDs) [18], organic field-effect transistors [19,20], non-linear optical materials [21,22], and xerography [23,24]. In addition, organic glasses of triphenylamine (TPA) derivatives have been widely investigated in the past two decades [19,25]. Considerable efforts in synthetic chemistry, in particular from Shirota and co-workers, have led to the development of many classes of TPA-based compounds as hole-transporting or electroluminescent materials [19,20]. Owing to the noncoplanarity of the three phenyl substituents, triphenylamine derivatives can be viewed as 3D systems. The combination of triphenylamine and linear π-conjugated systems could be expected to result in amorphous materials with isotropic optical and charge-transport properties. In recent years, it has been established that the excellent photoelectric function of triarylamines is favorable for organic sensitizers, and a large number of triarylamine-based dyes as electron donors have been developed for organic field-effect transistors (OFETs) or organic solar cells [26–31]. In recent publications, the further development of the organic photovoltaic materials based on triarylamines and new synthetic methods as well as the application of starburst triarylamines as host emitting materials have been reported [32–34]. Star-shaped molecules containing a triphenylamine core and branches of oligophenylenes, 2-phenylthiophene, or fluorene have been examined [35–38].

In our previous work, bipolar quinoxaline derivatives based on a quinoxaline core with triphenylamine pendants have been synthesized [39]. The foregoing compounds may serve as excellent blue–green light-emitting materials with high thermal stability and high fluorescence quantum yields. Therefore, our continuing interest in suitable materials for OLEDs [40] has led to the introduction of the styryl units in the triphenylamine moiety in order to improve the hole-transporting ability and fluorescent quantum yield. Herein, we report on the synthesis and properties of a series of novel triphenylamine derivatives containing styryl units. The π-bridge is extended to conjugated styryl units. We believe that the skeleton of this π-bridge maintains a basically planar

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molecular structure, since planarity is commonly regarded as a positive structural factor in enhancing the molecular fluorescent properties. As expected, the emission colour of these compounds can be easily tuned from blue to green by introducing the styryl units and changing the number of triphenylamine moieties. Particularly, these compounds exhibit good HOMO levels (−5.36 to −5.71 eV), high fluorescence quantum yields and high thermal properties, all of which lead to promising applications in OLEDs.

2. Experimental

2.1. Chemicals and instruments

All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 295 K on a Varian INOVA 400 MHz or a Varian NMR System 300 MHz spectrometer using $CDCl_3$ or d_6-DMSO as solvent and TMS as internal standard. Infrared spectra were taken in KBr pellets using a Varian 1000-IR Spectrometer. UV–vis spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-2500 spectrofluorometer. HRMS data were measured using TOF-MS(EI) instrument and microTOF-Q(ESI) instrument. Elemental analyses of C, H and N were performed using an EA 1110 elemental analyzer. Thermal properties were determined under nitrogen on a SDT 2960 (heating rate of 20 °C min^{-1}) and a DSC 2010 instruments (scanning rate of 20 °C min^{-1}). Cyclic voltammetry was carried out on a Chi 1200A electrochemical analyzer with three-electrode cell (Platinum was used as working electrode and as counter electrode, and SCE (saturated calomel electrode) as reference electrode) in $CHCl_3$ solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte.

2.2. 4-(Diphenylamino)benzaldehyde (*4*)

Compound **4** was synthesized according to the literature [34]. Phosphorus oxychloride (1.6 mL, 17 mmol) was added dropwise to DMF (1.5 mL, 20 mmol) at 0 °C for 1 h, and the mixture was stirred for 1 h at this temperature. Triphenylamine **3** (3.68 g, 15 mmol) was added and the reaction mixture was stirred at 100 °C for 5 h, after which time, the mixture was cooled to room temperature, poured into ice water (50 mL) and carefully neutralized with sodium hydroxide (20%). The ensuing solution was extracted with dichloromethane (3 × 50 mL) and the organic phase was washed with water (2 × 50 mL) and dried over anhydrous sodium sulfate. After filtration, the solvent was removed. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10, v/v) to give **4** (2.63 g, 70.0%). M.p. 122–123 °C (lit. [41] 120–121 °C). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.69 (d, $J = 8.8$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 4H), 7.17–7.19 (m, 6H), 7.03 (d, $J = 8.8$ Hz, 2H).

2.3. 4-(Bis(4-iodophenyl)amino)benzaldehyde (*5*)

Under rapid stirring, **4** (2.73 g, 10 mmol) was dissolved in glacial acetic acid (10 mL) and KI (3.32 g, 20 mmol) and KIO_3 (6.42 g 30 mmol) were added; the reaction mixture was stirred for 3 h at 70 °C. After cooling, the solid was filtered off and washed thoroughly with water (50 mL) and dichloromethane (100 mL). The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution (10%) until pH ≈ 8, with a saturated $NaHSO_3$ solution, and with saturated brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was stirred for 15 min in boiling ethanol (50 mL); the solution was cooled, and the pure product was isolated by filtration (4.2 g, 80%). M.p. 142–143 °C (lit. [42] 142–143 °C). Yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.61–7.73 (m, 6H), 7.07 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 5.4$ Hz, 4H).

2.4. N,N-Diphenyl-4-bromoaniline (*6*)

Compound **6** was synthesized according to the literature [43]. **3** (27.1 g, 120 mmol) and NBS (21.4 g, 120 mmol) were dissolved in CCl_4 (500 mL) and the solution was refluxed for 4 h. The precipitated succinimide was filtered, and the solvent was evaporated from the solution. The remaining grey coloured oil was recrystallized from ethanol. The obtained white crystalline powder was dried in a vacuum (34.3 g, 94%). M.p. 113–114 °C (lit. [44] 112–114 °C). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.20 (m, 6H), 7.11–6.99 (m, 6H), 6.97–6.90 (m, 2H).

2.5. 4-((4-Bromophenyl)(phenyl)amino)benzaldehyde (*7*)

This compound was prepared according to the Vilsmeier formylation reaction [34] using **6** (4.5 g, 20 mmol), phosphorus oxychloride (4.8 mL, 51 mmol), and DMF (4.5 mL, 60 mmol). The mixture was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1/4, v/v) to afford **7** (3.80 g, 68%). M.p. 153–154 °C (lit. [45] 151–153 °C). Yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.71 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 0.8.7$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.14–7.21 (m, 3H), 7.02–7.06 (m, 4H). HRMS M^+: Calcd for $C_{19}H_{14}BrNO$: 351.0259, Found: 351.0244.

2.6. 4-(Diphenylamino)phenylboronic acid (*8*)

A solution of **6** (3.3 g, 10.0 mmol) in anhydrous THF (50 mL) was cooled to −78 °C n-BuLi (2.5 mol L^{-1} in hexane, 4.8 mL, 12.0 mmol) was slowly added dropwise at −78 °C for for 2 h. After complete addition, the reaction mixture was stirred at −78 °C for another 1 h. Then, triisopropyl borate (3.5 mL, 15.0 mmol) was added at once. The mixture was allowed to warm to room temperature for 15 h. The reaction was finally quenched with HCl (2.0 mol L^{-1}, 40 mL) and the mixture was poured into water (100 mL). After extraction with dichloromethane (3 × 100 mL), The organic layer was washed with brine, dried over $MgSO_4$, concentrated. Further purification by silica gel column chromatography (petroleum ether/dichloromethane, 2/1, v/v) afforded **8** as a white solid (1.61 g, 54%). M.p. 228–229 °C (lit. [46] 228–229 °C). White solid, ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.84 (s, 2H), 7.65–7.68 (d, $J = 8.4$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 4H), 7.00–7.08 (m, 6H), 6.87–6.89 (d, $J = 8.1$ Hz, 2H).

2.7. 4-(Biphenyl-4-yl(phenyl)amino)benzaldehyde (*10*)

Under a nitrogen atmosphere, a mixture of **7** (3.52 g, 10 mmol), $Pd(PPh_3)_4$ as catalyst (0.4 mmol) and the phenylboronic acid (**9**) (1.22 g, 10 mmol) was stirred in dry toluene (25 mL). 2 mol L^{-1} K_2CO_3 (aq) solution (5 mL) was added via a syringe and the ensuing reaction mixture was heated to reflux for 72 h. After cooling, the product was extracted with dichloromethane (3 × 50 mL), washed with water (2 × 100 mL), dried over $MgSO_4$, filtered, concentrated and further purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10, v/v). The pure compounds **10** were obtained (2.27 g, 65%). M.p. 112–113 °C. White solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.71 (d, $J = 8.7$ Hz, 2H), 7.54–7.61 (m, 4H), 7.43–7.47 (m, 4H), 7.19–7.38 (m, 4H), 7.00–7.15 (m, 4H). HRMS M^+: Calcd for $C_{25}H_{19}NO$: 349.1467, Found: 349.1464.

2.8. General procedure for the synthesis of the compounds (*11*, *12*, *15*)

These compounds were prepared according to the similar procedure for **10.**

4-(Dibiphenyl-4-ylamino)benzaldehyde (**11**): m.p. 112–114 °C. Yield 62%, white powder. ^{1}H NMR(300 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.75 (d, $J = 8.7$ Hz, 2H), 7.57–7.61 (m, 8H), 7.43–7.47 (m, 4H), 7.29–7.38 (m, 4H), 7.16 (d, $J = 8.4$ Hz, 2H). HRMS M$^+$: Calcd for $C_{31}H_{23}NO$: 425.1780, Found: 425.1782.

4-((4'-(Diphenylamino)biphenyl-4-yl)(phenyl)amino)benzaldehyde (**12**): m.p. 123–125 °C. Yield 55%, white powder. ^{1}H NMR(300 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.71 (d, $J = 8.7$ Hz, 2H), 7.54 (d, $J = 8.7$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 6.9$ Hz, 2H), 7.27–7.29 (m, 3H), 7.19–7.24 (m, 6H), 7.12–7.15 (m, 6H), 7.01–7.09 (m, 4H). HRMS M$^+$: Calcd for $C_{37}H_{28}N_2O$: 516.2202, Found: 516.2201.

4-(bis(4'-(Diphenylamino)biphenyl-4-yl)amino)benzaldehyde (**15**): m.p. 136–137 °C. Yield 50%, white powder. ^{1}H NMR(300 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.71 (s, 2H), 7.54 (s, 3H), 7.46 (s, 4H), 7.26 (m, 11H), 6.97–7.18 (m, 20H). HRMS M$^+$: Calcd for $C_{55}H_{41}N_3O$: 759.3250, Found: 759.3253.

2.9. 4-(Bis(4-(phenylethynyl)phenyl)amino)benzaldehyde (*14*)

4-(bis(4-Iodophenyl)amino)benzaldehyde **5** (5.25 g, 10 mmol), ethynylbenzene **13** (2.10 g, 21 mmol), copper (I) iodine (47 mg, 0.25 mmol), bis(triphenylphosphine) dichloropalladium(II) (0.18 mg, 0.25 mmol) and triethylamine (25 mL) in dry toluene (25 mL) were placed in a sealed flask under an argon atmosphere. The mixture was stirred at room temperature for 0.5 h and then heated to 80 °C. After stirring for 24 h at this temperature, the mixture was filtered and the filtrate concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10, v/v) (3.55 g, 75%). M.p. 110–112 °C. Yellow solid, ^{1}H NMR(400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.48–7.54 (m, 8H), 7.34–7.36 (m, 6H), 7.12–7.14 (m, 6H). HRMS M$^+$: Calcd for $C_{35}H_{23}NO$: 473.1780, Found: 473.1777.

2.10. General procedure for the synthesis of the compounds (*16*–*22*)

1a ((bromomethyl)benzene) (1 mmol) or **1b** (1,4-bis(bromomethyl)benzene) (1 mmol) and triethyl phosphite (3 mmol) were heated to reflux at 185 °C for 3 h with stirring. Excess triethyl phosphite was collected under reduced pressure at 69 °C (1.5 mm Hg) and the phosphonium salt **2** (**2a** = diethyl benzylphosphonate, **2b** = tetraethyl 1,4-phenylenebis(methylene)diphosphonate) was obtained. The corresponding triphenylamine aldehyde in dry DMF (5 mL) was added dropwise. NaOEt (0.34g, 5 mmol) was then added and the mixture heated to 60 °C for 2 h. The ensuing mixture was filtered and the solids washed with EtOH. Solids were dissolved in dichloromethane, washed in distilled H_2O, dried over $MgSO_4$ and the solvent was removed. The residue was chromatographed on a silica gel column (petroleum ether/dichloromethane, 4/1, v/v) to afford the pure product. The following compounds were obtained in this fashion:

(E)-N,N-diphenyl-4-styrylaniline (**16**) from (**4**) and (**2a**); m.p. 204–206 °C. Yield 78%, white powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.48–7.50 (m, 3H), 7.32–7.39 (m, 5H), 7.24–7.26 (m, 3H), 7.04–7.12 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 142.2, 132.5, 126.4, 124.2, 123.5, 123.0, 122.2, 122.1, 121.9, 121.2, 119.4, 118.5, 117.9 ppm. IR (KBr, cm^{-1}): 1587, 1491, 1326, 1278, 1173, 963, 822, 751, 694. HRMS M$^+$: Calcd for $C_{26}H_{21}N$: 347.1674, Found: 347.1674.

Anal. calc. for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03%, found: C, 89.48; H, 6.18; N, 4.34%.

4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(N,N-diphenylaniline) (**17**) from (**4**) and (**2b**); m.p. 140–141 °C. Yield 77%, yellow powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.01–7.07 (m, 11H), 7.10–7.13 (m, 10H), 7.24 (s, 3H), 7.29 (s, 3H), 7.38–7.41 (m, 5H), 7.47 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.9, 118.4, 119.4, 121.5, 121.5, 122.2, 122.75, 124.2, 126.4, 131.5, 142.2, 142.4 ppm. IR (KBr, cm^{-1}): 1589, 1492, 1384, 1279, 1109, 961, 832, 752, 695. HRMS M$^+$: Calcd for $C_{46}H_{36}N_2$: 616.2878, Found: 616.2895.

Anal. calc. for $C_{46}H_{36}N_2$: C, 89.58; H, 5.88; N, 4.54%, found: C, 90.03; H, 5.63; N, 4.34%.

4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(N,N-bis(4-(phenylethynyl)phenyl)aniline) (**18**) from (**14**) and (**2b**); m.p. 130–131 °C. Yield 78%, yellow powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.03–7.14 (m, 15H), 7.29–7.34 (m, 18H), 7.39–7.43 (m, 9H), 7.50–7.53 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 157.7, 155.5, 155.3, 136.9, 136.8, 135.0, 134.9, 129.4, 128.8, 128.7, 127.3, 127.2, 123.5, 123.4, 121.9, 121.8, 113.6, 113.2, 113.1, 112.8, 112.3, 112.1, 110.4, 110.2, 110.1, 109.9, 91.1 ppm. IR (KBr, cm^{-1}): 1589, 1504, 1318, 1280, 1163, 960, 829, 754, 688. HRMS M$^+$: Calcd for $C_{78}H_{52}N_2$: 1016.4130, Found: 1016.4234.

Anal. calc. for $C_{78}H_{52}N_2$: C, 92.09; H, 5.15; N, 2.75%, found: C, 92.41; H, 4.76; N, 2.82%.

N,N'-(4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(N-phenylbiphenyl-4-amine) (**19**) from (**10**) and (**2b**); m.p. 160–161 °C yield 75%, yellow powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.03–7.24 (m, 20H), 7.29–7.32 (m, 5H), 7.42–7.51 (m, 14H), 7.56–7.59 (m, 5H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 123.1, 123.3, 123.4, 123.9, 124.1, 124.2, 124.6, 126.3, 126.3, 127.8, 127.8, 129.0, 129.7, 129.8, 130.1, 134.2, 134.6, 139.7, 139.7, 146.8, 146.9, 147.2 ppm. IR (KBr, cm^{-1}): 1592, 1488, 1325, 1280, 1174, 1103, 962, 832, 759, 695. HRMS M$^+$: Calcd for $C_{58}H_{44}N_2$: 768.3504, Found: 768.3478.

Anal. calc. for $C_{58}H_{44}N_2$: C, 90.59; H, 5.77; N, 3.64%, found: C, 90.35; H, 5.53; N, 4.12%.

N,N'-(4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(N-(biphenyl-4-yl)biphenyl-4-amine) (**20**) from (**11**) and (**2b**); m.p. 165–166 °C. Yield 77%, yellow powder, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.61 (m, 31H), 7.29–7.35 (m, 4H), 7.15–7.24 (m, 13H), 6.99–7.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 141.5, 135.4, 131.5, 130.6, 126.8, 123.6, 122.7, 122.6, 122.3, 121.8, 121.5, 119.4, 118.9 ppm. IR (KBr, cm^{-1}): 1597, 1511, 1323, 1284, 1107, 958, 833, 762, 694. HRMS M$^+$: Calcd for $C_{70}H_{52}N_2$: 920.4130, Found: 920.4080.

Anal. calc. for $C_{70}H_{52}N_2$: C, 91.27; H, 5.69; N, 3.04%, found: C, 90.64; H, 5.96; N, 3.40%.

N4,N4'-(4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(N4,N4',N4'-triphenylbiphenyl-4,4'-diamine) (**21**) from (**12**) and (**2b**); m.p. 187–188 °C. Yield 75%, yellow powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.39–7.48 (m, 18H), 7.24–7.28 (m, 10H), 7.12–7.17 (m, 22H), 6.97–7.08 (m, 12H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.7, 147.4, 147.1, 146.6, 136.9, 135.4, 134.9, 131.9, 129.6, 129.5, 128.1, 127.6, 127.6, 126.9, 126.9, 124.9, 124.7, 124.6, 124.3, 123.9, 123.4, 123.1 ppm. IR (KBr, cm^{-1}): 1618, 1490, 1328, 1277, 1176, 1103, 961, 845, 768, 693. HRMS M$^+$: Calcd for $C_{82}H_{62}N_4$: 1102.4974, Found: 1102.4924.

Anal. calc. for $C_{82}H_{62}N_4$: C, 89.26; H, 5.66; N, 5.08%, found: C, 90.04; H, 5.36; N, 4.60%.

N4,N4'-(4,4'-(1E,1'E)-2,2'-(1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(N4-(4'-(diphenylamino)biphenyl-4-yl)-N4',N4'-diphenylbiphenyl-4,4'-diamine) (**22**) from (**15**) and (**2b**); m.p. 189–190 °C. Yield 70%, yellow powder, ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.42–7.50 (m, 29H), 7.24–7.29 (m, 13H), 7.12–7.21 (m, 35H), 7.01–7.07 (m, 11H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 148.0, 147.9, 147.3, 147.1, 146.5, 136.9, 135.5, 134.8, 132.1, 129.5, 128.1, 127.7, 127.6, 126.9, 124.8, 124.6, 124.3, 124.1, 123.1 ppm. IR (KBr, cm^{-1}): 1645, 1594, 1490, 1325, 1277, 1103, 962, 820, 752, 694. HRMS M^+: Calcd for $C_{118}H_{88}N_6$: 1588.7070, Found: 1588.7395.

Anal. calc. for $C_{118}H_{88}N_6$: C, 89.14; H, 5.58; N, 5.29%, found: C, 88.58; H, 5.59; N, 5.84%.

3. Results and discussion

Triphenylamine aldehydes **4** and **7** were prepared by a Vilsmeier formylation reaction of the corresponding triphenylamine with $POCl_3$ in DMF (Fig. 1). Triphenylamine aldehydes **4** were obtained in better yields than the reported yields in reference [34] when the ration of $POCl_3$/DMF (1/1.2, mmol/mmol) was changed. Phosphonium salt **2** was synthesized via an Arbusov reaction of compound **1** and triethyl phosphite (Fig. 1) [47]. Triphenylamine aldehydes **10**, **11**, **12** and **15** were made using a Pd(0) catalyzed Suzuki C–C coupling reaction (Figs. 1 and 2) [48]. Compound **5** was treated with **13** using a Sonogashira coupling reaction to obtain the desired π-conjugated aromatic aldehyde **14** in moderate yields (Fig. 2) [49]. Compounds **16**–**22** were obtained via the Wittig–Horner condensation of the phosphonium salt **2a**, **2b** and the requisite aromatic aldehydes using NaOEt as a base (Figs. 2 and 3) [50]. All of these new compounds were characterized by HRMS, ^1H NMR and ^{13}C NMR spectroscopy.

3.1. Thermal properties

Glass transition temperatures (T_g) and decomposition temperatures (T_d) were determined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively, using a heating rate of 20 °C min^{-1}. The glass transition temperatures of these compounds were observed at ca. 130–144 °C (Table 1), which is significantly higher than that of the commonly used hole-transporting material of 1,4-bis(1-naphthylphenylamino)biphenyl (NBP, Tg 98 °C) [51]. The TGA data reveal that the thermal stability of these compounds also seems to be encouraging. The thermal decomposition does not occur below 380 °C for all of these compounds except **16**. Thermal and morphological stabilities of the organic electroluminescent (EL) materials play an important role in OLEDs. The excellent thermal stability with high T_d and T_g readily leads to high-stability OLEDs and high morphological stability, which is favorable to improve the performance and lifetime of OLEDs during operation.

3.2. Optical properties

The absorption spectra of these compounds were measured in $CHCl_3$ with a concentration of about 1.0×10^{-5} mol L^{-1} and are summarized in Table 1. The absorption spectra of these compounds were complicated due to multiple overlapping broad bands (Fig. 4). The maximum UV–vis absorptions of the compounds **16**–**22** are

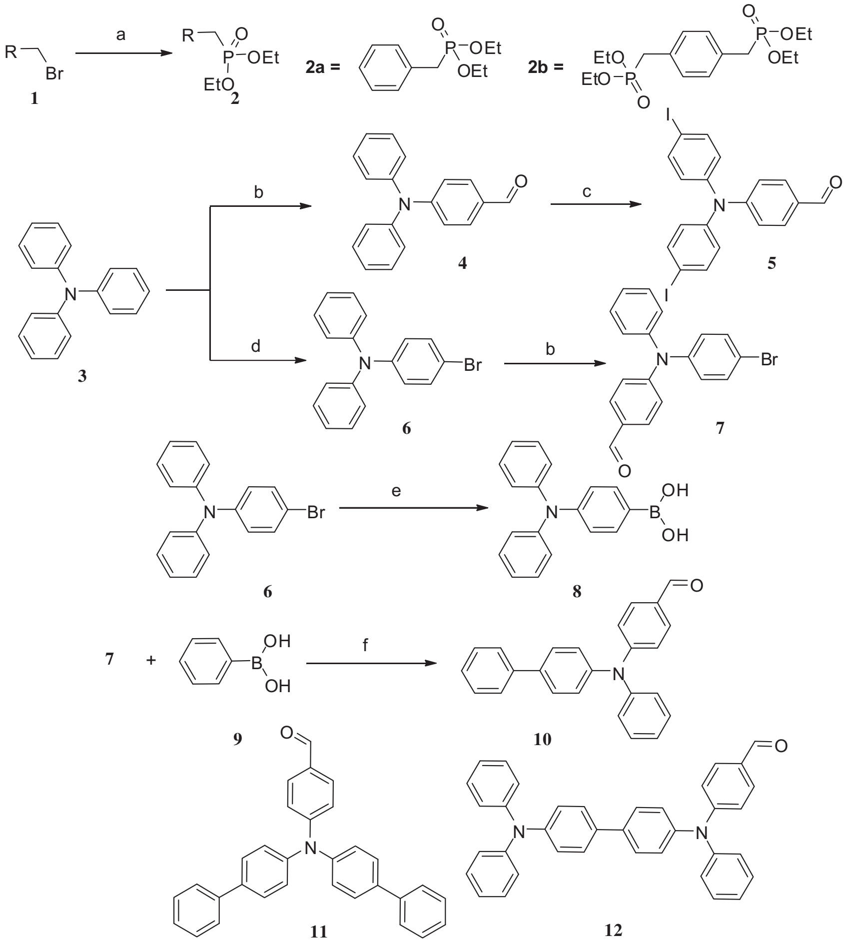

Fig. 1. Synthetic routines of the corresponding compounds: (a) $PO(OEt)_3$, 185 °C; (b) $POCl_3$, DMF, 0 °C, $CHCl_3$, 100 °C; (c) KIO_3/KI, HOAc, 100 °C; (d) NBS, CCl_4, 80 °C; (e) n-BuLi (1.2 equiv), THF, −78 °C, $(CH_3O)_3B$ (1.5 equiv), H_2O/HCl; (f) $Pd(PPh_3)_4$, K_2CO_3, toluene, 110 °C.

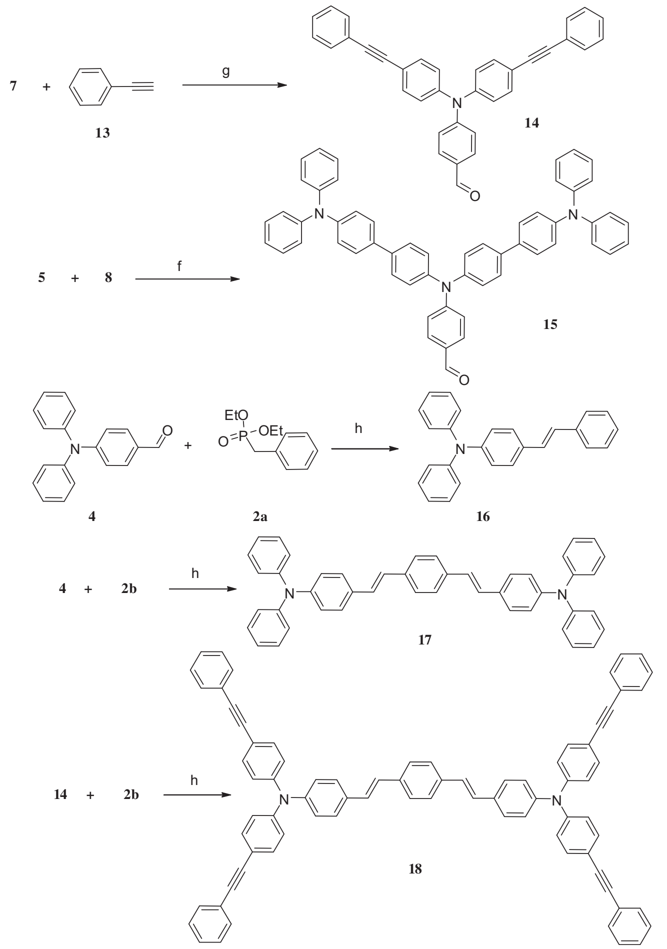

Fig. 2. Synthetic routines of the corresponding compounds: (f) $Pd(PPh_3)_4$, K_2CO_3, toluene, 110 °C; (g) $Pd[P(Ph)_3]_2Cl_2$, CuI, TEA, 80 °C; (h) NaOEt, DMF.

located in the range of 370–424 nm, which is ascribed to the π–π^* transition of the conjugated molecular backbone. Compound **16** exhibits a maximum absorption peak at 370 nm. The maximum absorption peak of compound **22** is red shifted to 424 nm, which indicates the formation of a more delocalized and extended π-conjugated system. The maximum absorption peaks of all compounds, except for **18** and **16**, are red shifted by 29–48 nm with respect to the (E)-4,4′-bis(diphenylamino)stilbene (BDPAS) [52]. In particular, in $CHCl_3$ solution the absorption maxima (λ_{max}) of the compound **18** are blue shifted by 4 and 51 nm corresponding to **16** and **20**, respectively which is ascribed to the incorporation of the acetylenyl benzene into the triphenylamine moieties, which increases the coplanarity of the molecule and minimizes steric interactions. This phenomenon is consistent with data reported by McIlroy et al., [53]. By inspecting the edge of the absorption spectra, the energy band gaps (Eg) of these compounds were obtained (Table 2) [54]. It was observed that the Eg values slightly decreased with the increment of the molecular length (increasing number of benzene and triphenylamine moieties). Moreover, the obvious difference between Eg of **18** (3.10 eV) and that of **16** (3.03 eV) indicated that the incorporation of the acetylenyl benzene into the triphenylamine moieties would result in different energy states of the whole molecules as result of the aforementioned the high coplanarity of the molecule and weak steric interactions.

PL emission spectra of **16**–**22** under excitation at 350 nm are presented in Fig. 5. These compounds afford a blue to green PL emission with the maximum emission peaks varying from 411 to 496 nm in $CHCl_3$. With increasing benzene and triphenylamine moieties, the PL emission peaks for **16**–**22** are gradually red shifted except for **18**. These are consistent with results from the UV-vis absorption spectra of these compounds. In the case of **18**, the

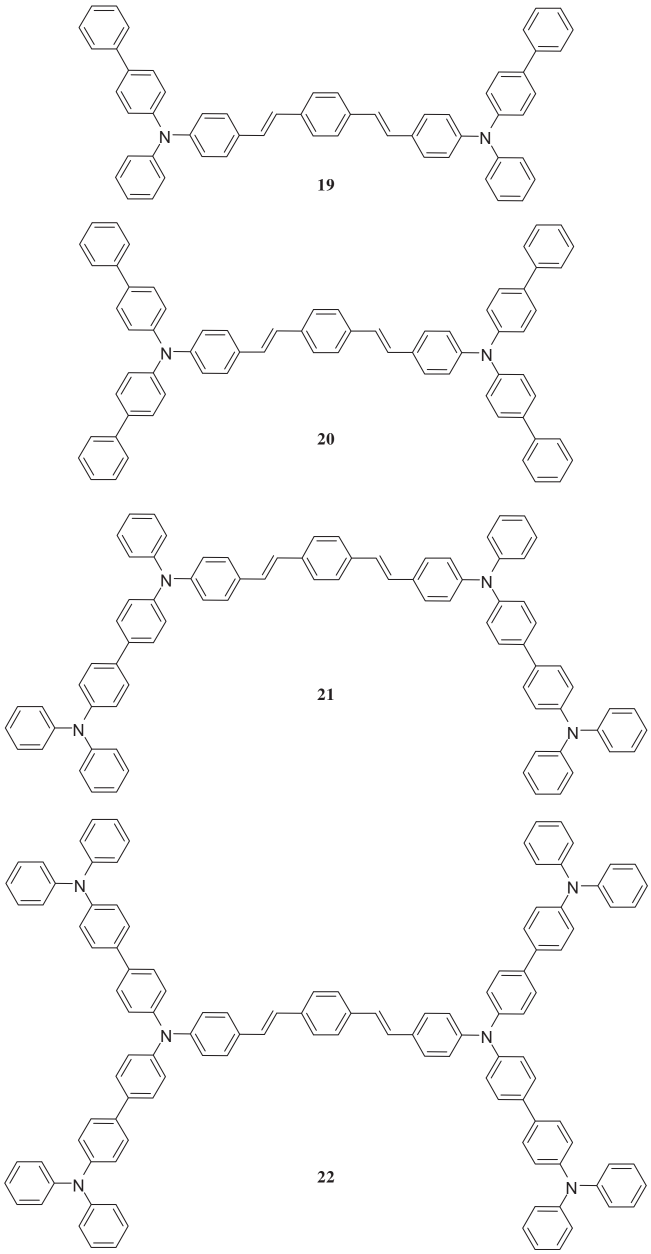

Fig. 3. Structures of compounds **19**–**22**.

Table 1
Optical properties of the compounds **16**–**22**.

compound	Abs. (nm)	em (nm)				Φ[a]
	$CHCl_3$	Toluene	$CHCl_3$	DMF	Solid	
(**16**)	370	414	438	455	450	0.12
(17)	411	460	468	499	529	0.28
(18)	366	404	411	437	564	0.40
(19)	412	462	470	497	585	0.10
(20)	417	467	478	503	532	0.39
(21)	416	468	483	509	522	0.35
(22)	424	475	496	516	531	0.65

[a] The fluorescence quantum yields (Φ) were measured in $CHCl_3$ using quinine sulfate (Φ = 0.55) as standard [23].

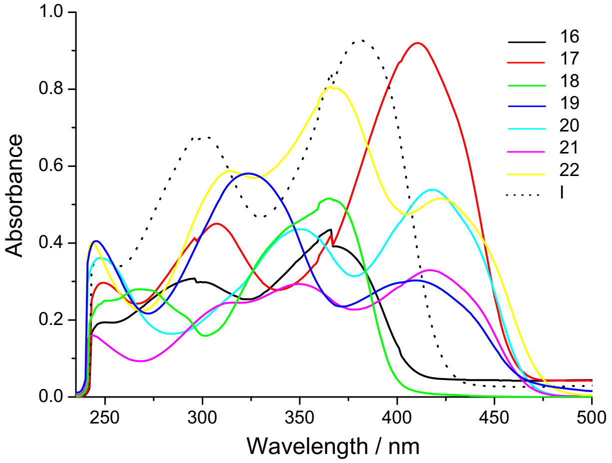

Fig. 4. The absorption spectra of compounds **16**–**22** (1×10^{-5} mol L^{-1} in $CHCl_3$).

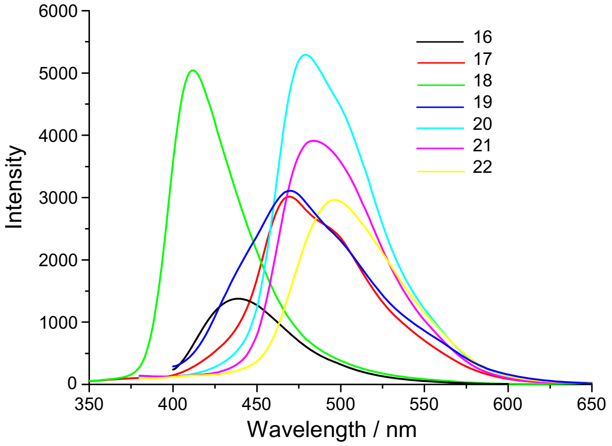

Fig. 5. Themission spectra of compounds **16**–**22** (1×10^{-6} mol L^{-1} in $CHCl_3$).

compound shows a blue fluorescence with the emission peak at 411 nm (Fig. 5) as result of the aforementioned high rigidity of its molecular structure. Further examination of the different emission behavior of these compounds (Fig. 6) indicated that these compounds show a larger red shift with increasing solvent polarity [55] and the results infer that these compounds are more polar in the excited state than in the ground state [56] and an increase in the polarity of the solvent will lower the energy level of the charge transfer excited state [52].

The emission spectra in the solid state were performed on powder coating on quartz substrates at room temperature. The shapes of the emission spectra in the solid state are correspondingly similar to those in $CHCl_3$ with bathochromic shifts in the emission wavelengths. As seen from Table 1, it seems that the incorporation of triphenylamine could reduce this bathochromic shift to some extent. For example, the emission of **20** in the solid state shows a red shift by 29 nm in comparison with that in $CHCl_3$, whereas the emission of **16** in the solid state shows a 12 nm red shift. The emission of **19** in the solid state shows a huge red shift of 115 nm which is ascribed to the facile formation of excimers between the phenyl groups of triphenylamine units, which cause a low-energy emission. Moreover, studies in solvents of different polarity also confirm that the blue shift of PL in $CHCl_3$ corresponding to that of the solid state is mainly due to the solvent effect [57–59]. This suggests that the polarized ground state on excitation undergoes a further reorganization to attain a more polar state, which results in interactions with a polar solvent for non-radiative relaxation to the ground state [57–59].

Table 2
Thermal and electrochemical properties of the compounds **16**–**22**.

compound	Band gap[a]	E_{HOMO}/ E_{LUM} (eV)[a]	E_g (eV)[b]	E_{ox}[c] (V)	E_{HOMO}/ E_{LUMO}[d] (eV)	T_d/T_g[e] (°C)
16	3.50	−4.82/−1.32	3.03	1.09	−5.49/−2.46	230/133
17	2.99	−4.62/−1.63	2.70	1.23	−5.63/−2.93	395/143
18	2.85	−4.73/−1.88	3.10	1.31	−5.71/−2.61	403/139
19	2.92	−4.63/−1.71	2.68	1.08	−5.48/−2.80	396/144
20	2.90	−4.65/−1.75	2.63	1.09	−5.49/−2.86	430/131
21	2.88	−4.57/−1.69	2.66	1.11	−5.51/−2.85	400/137
22	2.82	−4.52/−1.70	2.59	0.96	−5.36/−2.77	450/136

[a] DFT/B3LYP calculated values.
[b] Optical energy gaps calculated from the edge of the electronic absorption band.
[c] Oxidation potential in $CHCl_3$ (10^{-3} mol L^{-1}) containing 0.1 mol L^{-1} $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 100 mV s^{-1}.
[d] E_{HOMO} was calculated by $E_{ox} + 4.4$ V, and $E_{LUMO} = E_{HOMO} - E_g$.
[e] Measured by TG-DTA analysis under N_2 at a heating rate of 10 °C min^{-1}.

The fluorescence quantum yields (Φ) were measured in the $CHCl_3$ using quinine sulfate ($\Phi = 0.55$) as a standard (Table 1) [60]. The emission efficiency in dilute solution largely depends on the molecular structure. The PL quantum yields of the compounds are in the range of 0.10–0.65, which becomes higher with the increase in the number of the triphenylamine moieties and the molecular length. This difference of the quantum yields may appear during the process of the exciton migration [61], or result from the change of the molecular size [62]. The Φ value of 0.65 was observed for **22**, which is higher than that of recently reported compounds which are triphenylamine–thienylenevinylene hybrid systems (0.35) [31] and bis(phenanthroimidazolyl)biphenyl derivatives (0.54) [63].

3.3. Electrochemical properties

The electrochemical properties of compounds **16**–**22** were explored by cyclic voltammetry in $CHCl_3$ in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol L^{-1}) as the supporting electrolyte (Table 2). All of compounds **16**–**22** have one reversible oxidation peak which is an indication of a stable cation radical (Fig. 7). According to a reference to ferrocene (4.8 eV), the HOMO energy of these materials was calculated to get in the range of −5.36 to −5.71 eV [64,65]. Since the HOMO energy level is lower than that of the most widely used hole-transport material 4,4′-bis(1-naphthylphenylamino)biphenyl (NBP) (−5.20 eV, −2.4 eV),

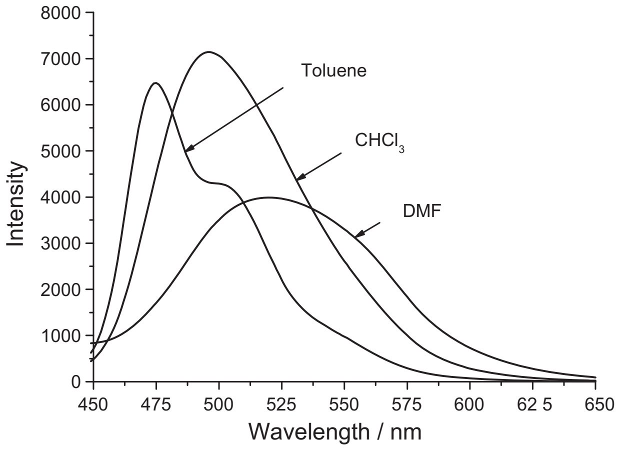

Fig. 6. The emission spectra of compound **22** in different solvents (1×10^{-6} mol L^{-1}) as sample.

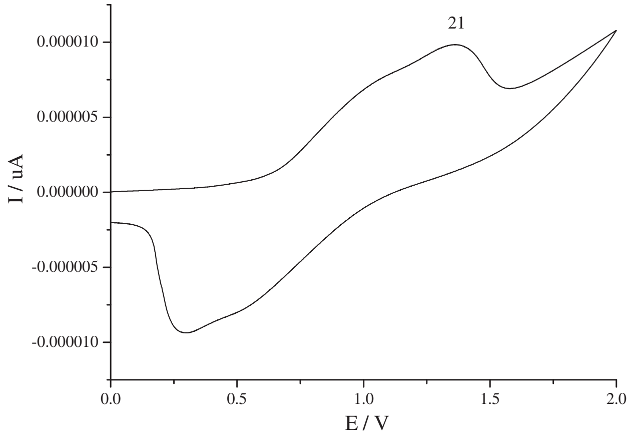

Fig. 7. Cyclic voltammogram of compound **21** (1×10^{-3} mol L^{-1}) as sample, in 0.1 mol L^{-1} Bu_4NPF_6–$CHCl_3$, scan rate 100 mV s^{-1}.

these materials might be beneficial for the hole-transporting [66]. Similarly, the optical edge was utilized to deduce the band gap and the LUMO energies. As expected, these compounds are of lower LUMO (−2.46 to −2.93 eV) energies and smaller band gaps compared with the other triphenylamine derivatives [66]. Their LUMO levels represent a small barrier for the electron injection from a commonly used cathode such as barium, with a work function of −2.2 eV [67]. In addition, the HOMO levels are in the range of −5.36 to −5.71 eV, which is close to that of the most commonly used hole-transport materials. Therefore, these compounds lead to improved hole hole-transporting and electron-transporting materials in applications for OLEDs [67].

3.4. Theoretical calculations

The electronic configurations were further examined using the theoretical models implanted in the Gaussian 03 program [68]. The calculations based upon Density Functional Theory (DFT) (B3LYP; 6-31G*) were carried out to obtain information about the HOMO and LUMO distributions of the compounds **16**–**22**. Due to the presence of the electron-rich amine moieties and an increase in the conjugation lengths, all of these compounds (Table 2) possess a high HOMO energy level (−4.52 to −4.82 eV), which could lead to impoved hole-transport properties [66]. The low LUMO energy of these compounds (−1.32 to −1.88 eV), which remains on the conjugated styryl units, is supposed to facilitate the acceptance of electrons from the cathode. It is generally indicative of a HOMO/LUMO absorption transition to bear a significant charge transfer character. According to the DFT calculations and the experimental data from the UV-absorption spectra, the calculated band gaps show a similar trend except for **18**. This exclusion may be attributed to increase the coplanarity of the compound **18** as a result of the incorporation of the acetylenyl benzene into the triphenylamine moiety [53]. The calculated HOMO/LUMO energy levels were higher than the corresponding estimations from the experimental data, a difference which may be related to various effects from conformations and solvents, which have not been taken into account here. Moreover, the electrochemistry is complicated owing to the reversibility of one of the redox processes; the accuracy of the Eg value is relatively limited [69].

4. Conclusions

In summary, a series of new aromatic diamines of different structural types have been prepared by a stepwise route involving a Pd(0) catalyzed Suzuki coupling reaction, Sonogashira coupling reaction and Wittig–Horner condensation reaction in good yields. The optical properties clearly indicate that the fluorescent emission properties of these compounds rely largely on the molecular structure. As expected, introduction of the styryl units and changing the number of triphenylamine moieties leads to a decrease in the optical band gaps. Moreover, these compounds exhibited high fluorescence quantum yields except for **16** and **19**, high glass transition temperatures from 130 to 144 °C and excellent luminescence emission from blue to green. The DFT calculations establish that they all possess a high HOMO energy level (−4.52 to −4.82 eV) due to the presence of the electron-rich amine moieties and increased conjugation lengths, giving rise to more balanced charge-transport characteristics, which indicate that these compounds are candidates for hole-transporting materials in OLED devices.

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