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The synthesis and characterization of novel dipolar fluorescent materials based on a quinoxaline core

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ABSTRACT

A series of dipolar quinoxaline derivatives with quinoxaline as core which carry pendant carbazole or triphenylamine moieties were synthesized and fully characterized. As expected, the compounds display bipolar character and can be explored as potential emissive and electron-transport materials as organic light-emitting diodes. Fluorescence spectra showed that the compounds exhibit excellent blue-green fluorescence.

1. Introduction

Organic fluorescent compounds have been extensively investigated for various potential applications including biological labels, photovoltaic cells, light-emitting diodes (LEDs), and optical sensors [1–5]. The nature of fluorescence depends largely on molecular structure and molecular assembly; in particular, materials that have both electron-donating and electron-accepting properties have recently received much attention owing to their potential application as organic light-emitting diodes (OLEDs); such materials must be able to accept both holes and electrons, that is, possess bipolar character [1].

Carbazole, triphenylamine and their derivatives have been widely utilized as a functional building block in the fabrication of the organic photoconductors, nonlinear optical materials, and photorefractive materials in OLEDs owing to their excellent solubility, stability and the excellent hole-transporting capability (the electron-donating properties) [6–22]. Similarly, quinoxaline is a useful n-type building block with high electron affinity (electron-accepting character) and good thermal stability. Moreover, quinoxaline has been successfully incorporated in small molecules and polymers as the electron-transport component of OLEDs [23–27]. However, in contrast to the vast literature on donor/acceptor materials, quinoxaline-containing triarylamines, as potential hole-transporting and emitting materials for organic electroluminescent (EL) devices, have received little attention [24]; materials bearing a quinoxaline core and carbazole or triphenylamine pendants have not been explored. In a continuation of our interest in materials suitable for OLEDs [28,29], this paper concerns the synthesis and properties of a series of novel dipolar quinoxaline derivatives.

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. ^{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 $CDCl_3$ as solvent and TMS as internal standard. UV–vis spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-2500 spectrofluorometer. Mass spectroscopic (MS) measurements were carried using matrix-assisted laser desorption ionisation-time-of-flight (Voyager-DE STR MALDI-TOF) technique. HRMS data were measured using TOF-MS (EI$^+$) instrument. Cyclic voltammetry was carried on a Chi 1200A

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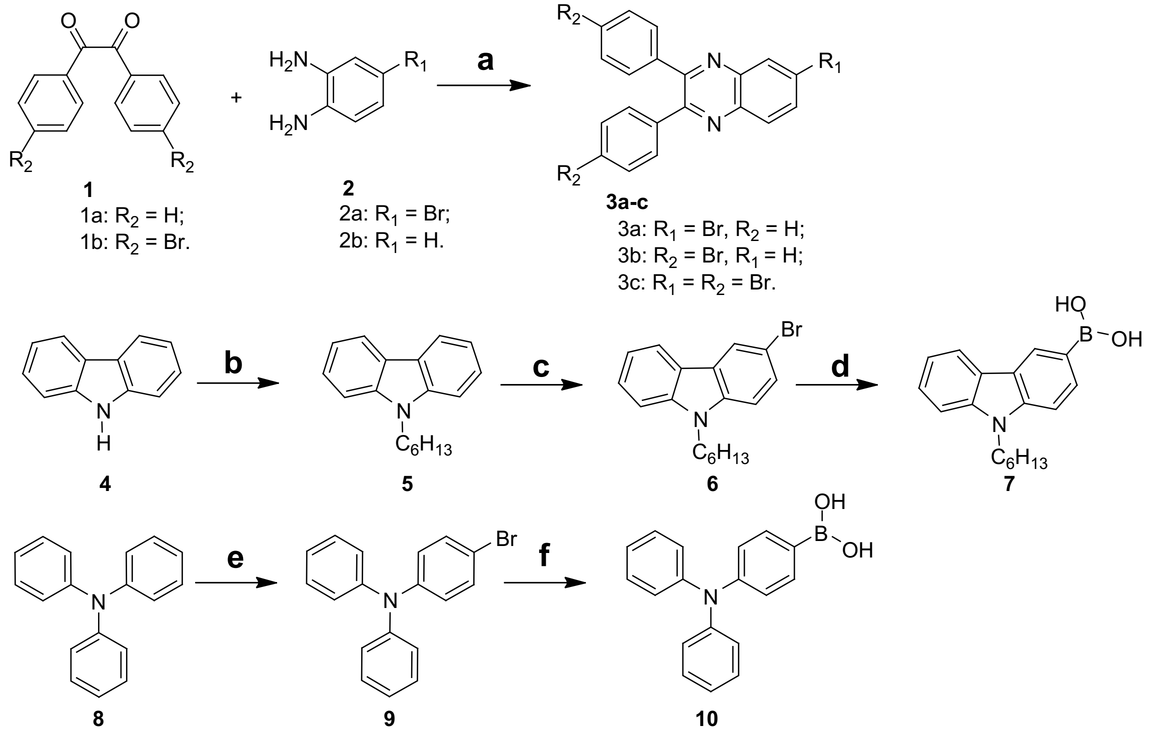

Fig. 1. Synthetic routes for compounds **3a–c**, **7** and **10**. *Reagents and conditions*: (a) *p*-toluenesulfonic acid, $CHCl_3$, 60 °C; (b) carbazole:1-bromohexane = 1:1.1, KOH, tetrabutylammonium bromide, DMSO, 100 °C; (c) 9-hexyl-9*H*-carbazole:NBS = 1:1, $CHCl_3$, dark, 0 °C; (d) *n*-BuLi (1.2 equiv), THF, −78 °C, $(CH_3O)_3B$ (1.5 equiv), H_2O/HCl; (e) triphenylamine:NBS = 1:1, CCl_4, 80 °C; (f) *n*-BuLi (1.2 equiv), THF, −78 °C, $(CH_3O)_3B$ (1.5 equiv), H_2O/HCl.

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 CH_2Cl_2 solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte. Thermal properties were performed on an SDT 2960 and a DSC 2010 instruments. Melting points were measured using an XT-5 apparatus.

2.2. 6-Bromo-2,3-bis(4-bromophenyl)quinoxaline (*3c*)

Under a nitrogen atmosphere, a mixture of 1,2-bis(4-bromophenyl)ethane-1,2-dione **1b** (3.68 g, 10.0 mmol), 4-bromo-1,2-diaminobenzene **2a** (1.87 g, 10.0 mmol), and *p*-toluenesulfonic acid (50 mg) in $CHCl_3$ (30 mL) was refluxed for 48 h. The solution was cooled to room temperature and filtered. The solvent was subsequently evaporated under reduced pressure, and the residue was recrystallized from acetonitrile to afford compound **3c** as a yellow solid (3.63 g, 70%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, $J = 8.0$ Hz, 4H), 7.50 (d, $J = 8.0$ Hz, 4H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.9 (d, $J = 12.0$ Hz, 1H), 8.33 (s, 1H).

2.3. 9-Hexylcarbazole (*5*)

To a stirred solution of carbazole **4** (20.0 g, 120 mmol) and tetrabutylammonium bromide (TBAB) (0.8 g) in DMSO (100 mL) was added 70.0 g 50% KOH (aq). Then hexylbromide (23.1 g, 140 mmol) was added dropwise. After complete addition, the reaction mixture was refluxed for 16 h. The organic layer was separated, washed with water, dried over $MgSO_4$ and concentrated. Pure product was obtained after column chromatography (silica gel, hexane/triethylamine, 98/2, v/v) as a white solid (27.7 g, 92%).

^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.28–1.40 (m, 6H), 1.81–1.91 (m, 2H), 4.30 (t, $J = 6.8$ Hz, 2H), 7.20–7.24 (m, 2H), 7.39–7.50 (m, 4H), 8.10 (d, $J = 7.6$ Hz, 2H).

2.4. 3-Bromo-9-hexylcarbazole (*6*)

In a flask, covered with aluminum foil, a stirred solution of 9-hexylcarbazole **5** (5.02 g, 20.0 mmol) in $CHCl_3$ (100 mL) was cooled to 0 °C. *N*-Bromosuccinimide (NBS; 3.56 g, 20.0 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. $CHCl_3$ was evaporated and the crude product was purified by extraction with diethylether and water. After same work up as above, final product was obtained as white crystals (2.31 g, 70%).

^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.28–1.39 (m, 6H), 1.77–1.87 (m, 2H), 4.23 (t, $J = 6.8$ Hz, 2H), 7.23–7.26 (m, 2H), 7.36–7.53 (m, 3H), 8.02 (d, $J = 7.2$ Hz, 1H), 8.19 (s, 1H).

2.5. 9-Hexylcarbazol-3-ylboronic acid (*7*)

A solution of 3-bromo-9-hexylcarbazole **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. After complete addition, the reaction mixture was stirred 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 a large amount of water. After extraction with CH_2Cl_2 (3×20 mL), The organic layer was washed with brine, dried over $MgSO_4$, concentrated. Further purification by column chromatography (silica gel, hexane/dichloromethane, 2/1, v/v) afforded the product as a white solid (1.61 g, 54%).

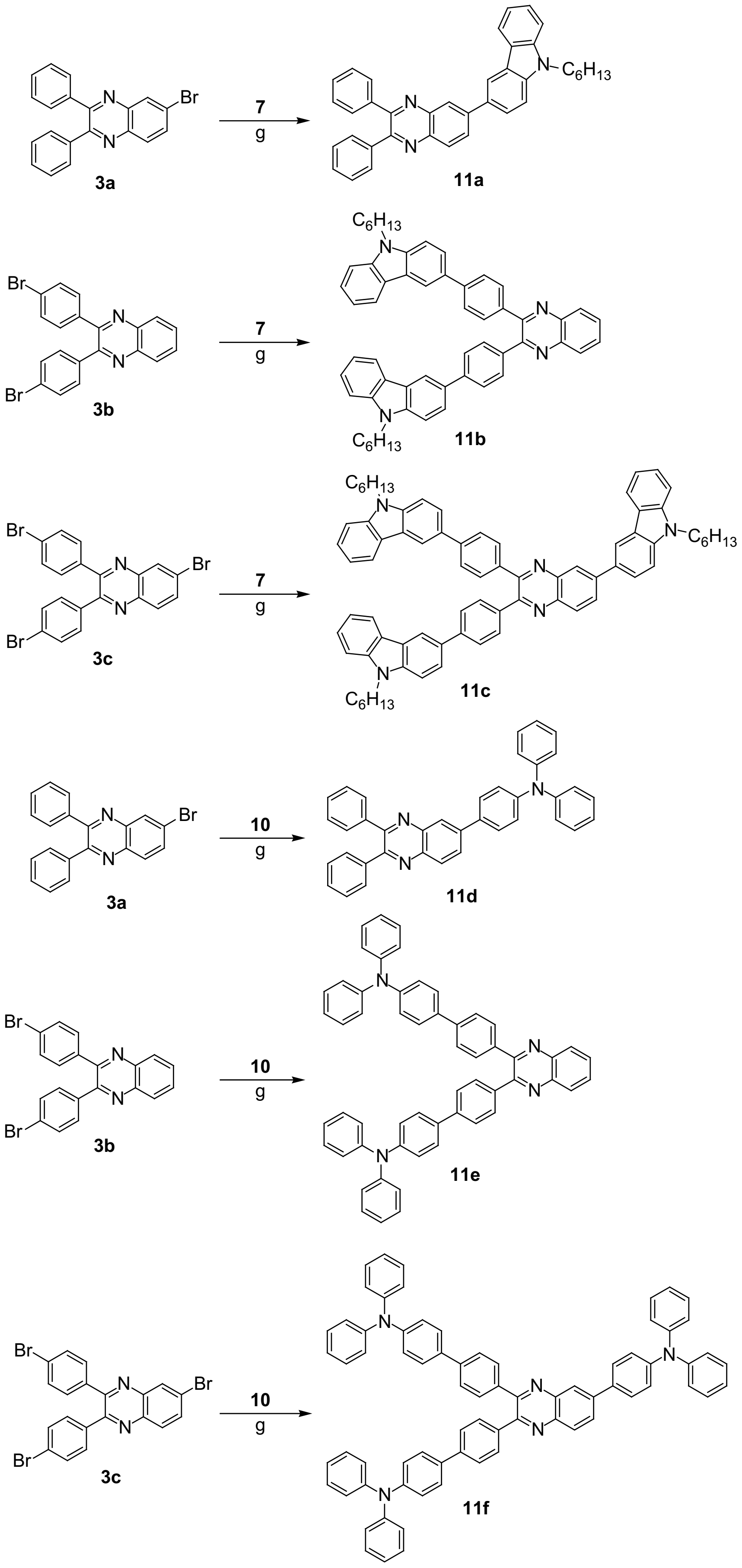

Fig. 2. Synthetic routes of **11a–f**. *Reagents and conditions*: (g) cat. $Pd(PPh_3)_4$, 2 mol L^{-1} K_2CO_3, toluene, 80 °C.

Table 1
Optical, thermal, and electrochemical properties of compounds **11a**–**f**.

Compounds	abs (nm)	em (nm)		Φ	E_g (eV)	E_{pa} (V)	E_{pc} (V)	HOMO/LUMO (eV)	T_m/T_d (°C)
	DCM	DCM	Solid						
11a	380	498	500	0.52	2.89	0.81	–[a]	−5.21/−2.32	109/410
11b	392	496	462	0.44	2.82	0.80	0.77	−5.20/−2.38	170/475
11c	404	493	494	0.60	2.68	0.80	0.76	−5.20/−2.52	191/480
11d	351	552	494	0.23	2.69	0.99	0.93	−5.39/−2.70	189/400
11e	384	559	507	0.06	2.75	0.98	0.91	−5.38/−2.63	114/410
11f	410	560	510	0.78	2.58	0.98	0.91	−5.38/−2.80	140/450

[a] Not available.

^{1}H NMR (300 MHz, d_6-DMSO): δ 0.78 (t, J = 6 Hz, 3H), 1.24–1.35 (m, 6H), 1.73–1.75 (m, 2H), 4.36 (t, J = 6.0 Hz, 2H), 7.20 (t, J = 6 Hz, 1H), 7.40–7.58 (m, 3H), 7.90 (s, 2H), 7.92 (s, 1H), 8.09 (d, J = 6.0 Hz, 1H), 8.60 (s, 1H).

2.6. 4-Bromo-N,N-diphenylaniline (*9*)

A mixture of triphenylamine **8** (29.4 g, 120 mmol) and NBS (21.4 g, 120 mmol) in CCl_4 (500 mL) was refluxed for 4 h. The precipitated succinimide was filtered, and the solvent was evaporated from the solution. The remaining gray oil was recrystallized from ethanol. The white crystalline powders were obtained (36.2 g, 93%).

^{1}HNMR (400 MHz, $CDCl_3$): δ 6.97–6.90 (m, 2H), 7.11–6.99 (m, 6H), 7.35–7.20 (m, 6H).

2.7. 4-(Diphenylamino)phenylboronic acid (*10*)

Compound **10** was prepared following a method similar to compound **7**.

Compound **10**: yield 55%, white. ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.88 (d, J = 6.0 Hz, 2H), 7.00–7.08 (m, 6H), 7.30 (t, J = 6.0 Hz, 4H), 7.66 (t, J = 9.0 Hz, 2H), 7.84 (s, 2H).

2.8. General procedure for the synthesis of compounds (*11a*–*f*)

Under a nitrogen atmosphere, a mixture of compounds (**3a**–**c**) (1.0 mmol), $Pd(PPh_3)_4$ catalyst (0.04 mmol) and the corresponding carbazole (or triphenylamine) boronic acid (**7** or **10**) was stirred in dry toluene (15 mL). Then, 2 mol L^{-1} K_2CO_3 (aq) solution (2 mL) was added via syringe. The reaction mixture was heated to reflux for 72 h. After cooling, the product was extracted with DCM, washed with water, dried over $MgSO_4$, filtered, concentrated and further purified by column chromatography (silica gel, hexane/dichloromethane, 10/1, v/v). The pure compounds **11a**–**f** were obtained.

2.8.1. 6-(9-Hexylcarbazole-3-yl)-2,3-diphenylquinoxaline (*11a*)

Yield 61%, yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.30–1.43 (m, 6H), 1.923 (t, J = 7.2 Hz, 2H), 4.35 (t, J = 6.8 Hz, 2H), 7.73–7.56 (m, 14H), 7.92 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 8.24–8.28 (m, 2H), 8.52 (s, 1H), 8.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.5, 23.0, 27.5, 29.5, 32.1, 43.7, 77.5, 109.4, 109.7, 119.7, 119.8, 120.9, 123.4, 124.1, 125.7, 126.3, 126.5, 128.85, 129.2, 129.2, 129.8, 130.4, 130.5, 130.9,139.7, 139.7, 140.9, 141.4, 142.2.

HRMS [Found: m/z 531.2680 (M^+), Calcd for $C_{38}H_{33}N_3$: M, 531.2674].

2.8.2. 2,3-Bis(4-(9-hexylcarbazol-3-yl)phenyl)quinoxaline (*11b*)

Yield 58%, yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 6.4 Hz, 6H), 1.29–1.39 (m, 12H), 1.87 (t, J = 6.8 Hz, 4H), 4.31 (t, J = 6.8 Hz, 4H), 7.21 (d, J = 7.2 Hz, 2H), 7.39–7.46 (m, 6H), 7.74–7.76 (m, 12H), 8.12 (d, J = 7.6 Hz, 2H), 8.21 (s, 2H), 8.36(s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.8, 27.2, 29.2, 31.8, 43.5, 77.3, 109.1, 109.2, 119.1, 119.2, 120.7, 123.2, 123.6, 125.3, 126.1, 127.3, 129.4, 130.1, 130.6, 131.5, 137.4, 140.4, 141.1, 141.5, 142.8, 153.6.

HRMS [Found: m/z 780.4174 (M^+), Calcd for $C_{56}H_{52}N_4$: M, 780.4192].

2.8.3. 6-(9-Hexylcarbazol-3-yl)-2,3-bis(4-(9-hexylcarbazol-3-yl)phenyl)quinoxaline (*11c*)

Yield 51%, yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85–0.91 (m, 9H), 1.31–1.42 (m, 18H), 1.85–1.95 (m, 6H), 4.31–4.38 (m, 6H), 7.22–7.24 (m, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.41–7.57 (m, 10H), 7.78 (s, 9H), 7.75 (d, J = 8.0 Hz, 1H), 8.14–8.32 (m, 5H), 8.38 (s, 2H), 8.55(s, 1H), 8.58 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.8, 27.2, 29.2, 31.8, 43.4, 77.2, 109.1, 109.2, 109.5, 119.1, 119.2, 119.4, 119.6, 120.7, 123.2,

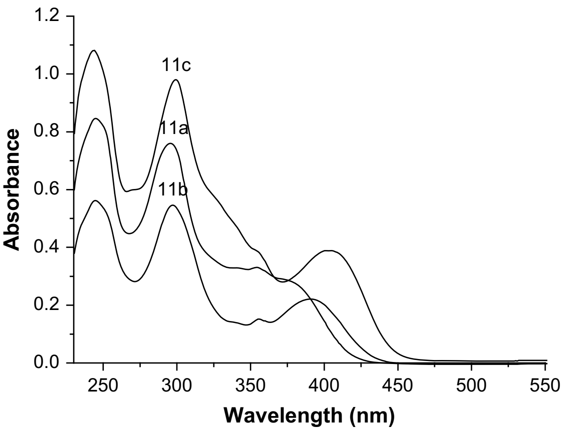

Fig. 3. The absorption spectra of compounds **11a**–**c** (1×10^{-5} mol L^{-1} in CH_2Cl_2).

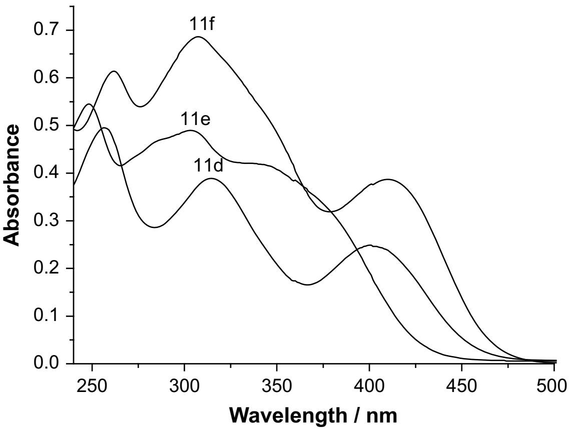

Fig. 4. The absorption spectra of compounds **11d**–**f** (1×10^{-5} mol L^{-1} in CH_2Cl_2).

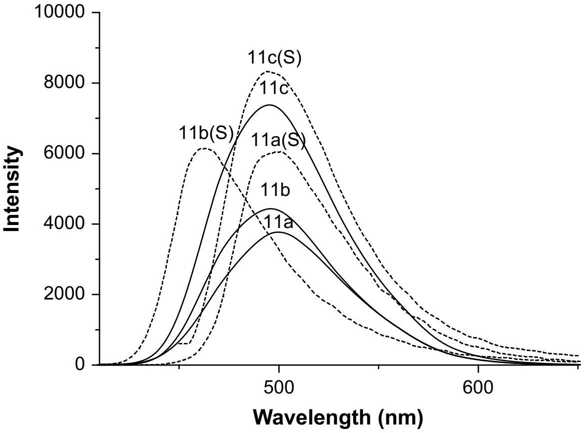

Fig. 5. The emission spectra of compounds **11a–c** (1×10^{-5} mol L^{-1} in CH_2Cl_2). The dashed line showed the emission spectra of solid compounds **11a–c**.

123.6, 123.8, 125.3, 125.5, 126.0, 126.1, 126.2, 127.3, 129.6, 130.1, 130.6, 130.8, 131.6, 137.5, 137.6, 140.4, 140.6, 140.7, 141.1, 141.2, 141.9, 142.6, 142.7, 143.7, 152.8, 153.8.

MS (MALDI-TOF) [Found: *m*/*z* 1031.0 (M$^+$), Calcd for $C_{74}H_{71}N_5$: M, 1029.6].

2.8.4. 6-N,N-*Diphenylaniline-4-yl-2,3-diphenylquinoxaline* (***11d***)

Yield 61%, yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, $J = 7.2$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 6H), 7.30–7.35 (m, 10H), 7.52 (d, $J = 6.0$ Hz, 4H), 7.67 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 8.4$ Hz, 1H), 8.19 (d, $J = 8.8$ Hz, 1H), 8.36 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.3, 123.6, 125.1, 125.6, 128.3, 128.5, 128.9, 129.0, 129.5, 129.6, 130.1, 133.2, 139.4, 139.4, 140.6, 141.8, 142.3, 147.7, 148.4, 153.2, 154.1.

HRMS [Found: *m*/*z* 525.2206 (M$^+$), Calcd for $C_{38}H_{27}N_3$: M, 525.2205].

2.8.5. 2,3-*Bis(4-*N,N-*diphenylaniline-4-yl)-phenylquinoxaline* (***11e***)

Yield 52%, yellow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02–7.14 (m, 20H), 7.41–7.64 (m, 16H), 7.78 (s, 2H), 8.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.5, 123.3, 123.5, 123.5, 124.2, 124.8, 124.9, 126.8, 126.9, 128.2, 129.6, 129.7, 129.8, 130.8, 131.9, 132.0,148.0.

HRMS [Found: *m*/*z* 768.3228 (M$^+$), Calcd for $C_{56}H_{40}N_4$: M, 768.3253].

2.8.6. 6-(N,N-*Diphenylaniline-4-yl)-2,3-bis(4-*N,N-*diphenylaniline-4-yl)-phenylquinoxaline* (***11f***)

Yield 51%, orange red. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–7.69 (m, 50H), 8.06 (s, 1H), 8.19 (m, 1H), 8.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.3, 122.9, 123.3, 123.3, 123.6, 123.6, 123.7, 124.0, 124.4, 124.7, 124.7, 124.8, 125.1, 125.5, 125.6, 126.6, 126.6, 126.7, 127.9, 128.2, 128.3, 129.4, 129.6, 129.6, 130.5, 131.7, 131.7, 131.8, 131.9, 147.6, 147.8.

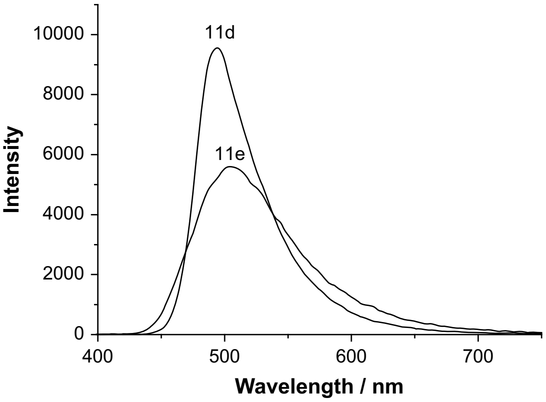

Fig. 7. The emission spectra of solid compounds **11d–e**.

MS (MALDI-TOF) [Found: *m*/*z* 1012.1 (M$^+$), Calcd for $C_{74}H_{53}N_5$: M, 1011.4].

3. Results and discussion

Compounds **3a–c**, **7** and **10** were synthesized according to methods described in literature [24,19,28] (Fig. 1). For products **11a–f**, the carbazole or triphenylamine moiety was introduced via a Pd(0) catalyzed Suzuki C–C coupling reaction [30] (Fig. 2).

3.1. Thermal properties

The thermal properties of these compounds were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the detailed data are listed in Table 1. The experiment results revealed that the thermal stability of these compounds also seems to be encouraging. The thermal decomposition of these compounds does not occur below 400 °C. The T_m and T_d values for tri-carbazole moiety pendants are higher than those of di-carbazole and di-triphenylamine moieties or single carbazole moiety pendants. Rising T_m and T_d because of the presence of carbazole moieties in amorphous molecules is well documented in literature [6,31]. However, the T_m for single triphenylamine moiety incorporation quinoxaline moiety is higher than tri- and di-triphenylamine moieties as pendants. This may be due to

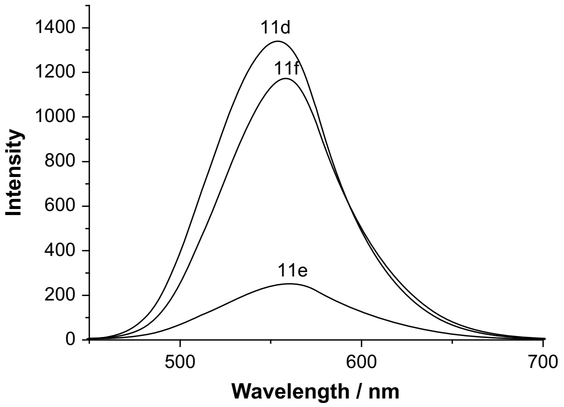

Fig. 6. The emission spectra of compounds **11d–f** (1×10^{-5} mol L^{-1} in CH_2Cl_2).

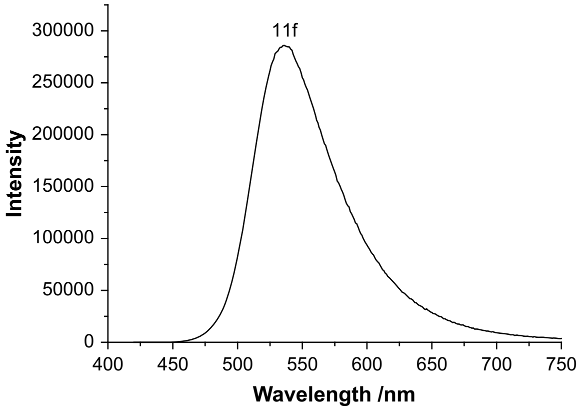

Fig. 8. The emission spectra of solid compounds **11f**.

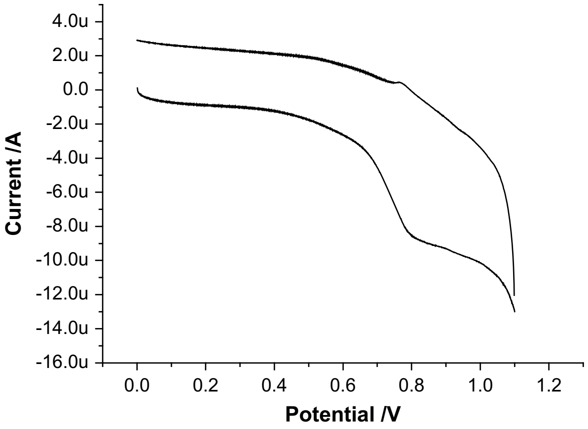

Fig. 9. Cyclic voltammogram of **11c** (0.5×10^{-3} mol mol L^{-1}) as sample, in 0.1 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}.

triphenylamine moiety linked quinoxaline at different positions, which affected the symmetry of compounds.

3.2. Optical properties

The UV–vis absorption and photoluminescent (PL) properties of compounds **11a**–**f** in dilute solutions and in the solid state are presented in Table 1. As shown in Figs. 3 and 4, absorption spectra of each compounds exhibit intense absorption bands which are attributed to the π–π^* transition of the conjugated backbone [24]. The absorption maxima (λ_{max}) of **11a** were at 380 nm. By increasing the number of carbazole moieties, the absorption maxima (λ_{max}) of compounds **11b**–**c** are red shifted to 392, and 404 nm, which indicated the formation of a more delocalized and extended π-conjugated system. Spectra of compounds **11d**–**f** showed a maximum absorption peak at 401, 372, and 410 nm, respectively. The absorption maxima (λ_{max}) of **11e** are blue shifted to 372 nm relative to other compounds, which may be due to the symmetry of di-triphenylamine moieties containing quinoxaline is the highest in all of compounds. The π–π^* energy gaps (E_gs) of these compounds were calculated from the UV–vis absorption threshold [31]. It was obvious that the E_gs of compounds could be greatly reduced by increasing the number of carbazole or triphenylamine moieties as the pendant of compound backbone except **11e** (Table 1).

Fig. 5 displays the PL emission spectra of compounds **11a**–**c** excited at 390 nm. These compounds showed a blue-green PL emission with the maximum emission peaks varying from 494 to 500 nm in CH_2Cl_2 solutions. With the increasing of carbazole moieties, the fluorescence intensity for **11a**–**c** is gradually enhanced. In the case of **11d**–**f**, these compounds showed a green fluorescence with the maximum emission peaks varying from 554 to 560 nm in CH_2Cl_2 (Fig. 6). In the solid state, compounds **11b** (Fig. 5) and **11d**–**f** (Figs. 7 and 8) exhibit a significant blue shift in their fluorescence emission. The maximum emission peaks of solid **11b** and **11d**–**f** are blue shifted by 34, 58, 52 and 50 nm, respectively (Table 1), due to the pronounced steric crowding in **11d**–**f**, which results in less coplanarity of the molecule [32]. Moreover, studies with solvents of different polarity also confirmed that the red shift of PL in solution (CH_2Cl_2) relative to the solid state is mainly due to the solvent effect [6]. Those solid emissions are significantly enhanced, typically for the case of **11d**–**f** (Figs. 6–8) in comparison with its emission in CH_2Cl_2. This suggests that the polarized ground state on excitation undergoes further reorganization to attain a more polar state, which on interaction with a polar solvent relaxes to the ground state nonradiatively [24].

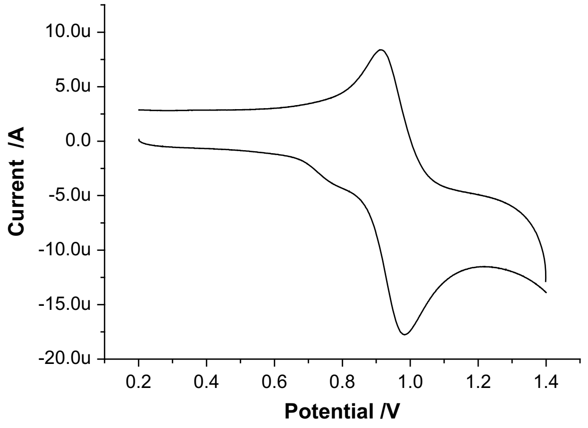

Fig. 10. Cyclic voltammogram of **11f** (0.5×10^{-3} mol L^{-1}) as sample, in 0.1 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}.

The PL quantum yields (Φ) were measured in CH_2Cl_2 using Rhodamine-6G ($\Phi = 0.595$) as standard [31]. The highest Φ value of 0.78 was observed for **11f**, which is higher than that of small molecules and polymers containing quinoxaline units [24–26]. The difference of quantum yields might be happened during the process of exciton migration [33] or might be due to the change of the molecular size [34].

3.3. Electrochemical properties

The electrochemical properties of compounds **11a**–**f** were analyzed by cyclic voltammetry in CH_2Cl_2 solution in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol L^{-1}) as supporting electrolyte and the results are listed in Table 1. The carbazole-containing compound **11a** displays an irreversible oxidation peak, which might be due to the formation the corresponding cation radical by a fast dimerization at position 3 of the carbazole units [34]. Compounds **11b**–**f** show one reversible oxidation peak indicative of stable cation radical (Figs. 9 and 10). The energy of the HOMO of these materials was calculated with reference to ferrocene (4.8 eV) and ranges from −5.20 to −5.38 eV [35,36]. 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) and thus might be beneficial for the hole-transport capacity [37]. Similarly, the optical edge was utilized to derive the band gap and the LUMO energies. As expected, these compounds by using quinoxaline as core possess lower LUMO energies and smaller band gaps compared to the simple quinoxaline derivatives [27]. The values (−2.32 to −2.80 eV) are slightly higher than that observed for quinoxaline monomers [23] and quinoxaline heterocycle hybrid polymers [38]. It suggested that quinoxaline-containing carbazole or triphenylamine is responsible for the rise in the LUMO level. Their LUMO levels represented a small barrier for electron injection from a commonly used cathode such as barium, which has a work function of −2.2 eV [12,39]. Moreover, HOMO levels were in the range of −5.20 to −5.38 eV, which is near the most widely used hole-transport materials. Therefore, these compounds might be used for hole-transporting and electron-transporting materials for OLEDs [39–42].

4. Conclusions

In summary, a series of the novel quinoxaline derivatives as potential hole-transporting and emitting materials for OLED, were synthesized by a stepwise route involving a Pd(0) catalyzed Suzuki coupling reaction in good yields. As is believed, it is possible to obtain three-in-one molecules possessing hole-transporting and emitting and electron-transporting characteristics by using quinoxaline as core and carbazole or triphenylamine as pendant in the future. Work towards improving the electron carrier capability of quinoxaline segments by the incorporation of electron-withdrawing groups such as cyano- or perfluoroarene is currently underway in our laboratory.

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References

[1] Mullen K. Organic light emitting devices: synthesis, properties and applications. Weinheim, Germany: Wiley-VCH; 2006.

[2] Tang CW, Vanslyke SA. Organic electroluminescent diodes. Applied Physics Letters 1987;51(12):913–5.

[3] Berresheim AJ, Muller M, Mullen K. Polyphenylene nanostructures. Chemical Reviews 1999;99(7):1747–85.

[4] Hide F, Diaz-Garcia MA, Schartz BJ, Heeger AJ. New developments in the photonic applications of conjugated polymers. Accounts of Chemical Research 1997;30:430–6.

[5] Kraft A, Grimsdale AC, Holms AB. EL conjugated polymers – seeing polymers in a new light. Angewandte Chemie International Edition 1998;37(4):402–28.

[6] Thomas KRJ, Lin JT, Tao YT, Ko CK. Light-emitting carbazol derivatives: potential electroluminescent materials. Journal of the American Chemical Society 2001;123(38):9404–11.

[7] Brunner K, Dijken AV, Börner H, Bastiaansen JJAM, Kiggen NMM, Langeveld BMW. Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: tuning the HOMO level without influencing the triplet energy in small molecules. Journal of the American Chemical Society 2004;126(19):6035–42.

[8] Zhang Y, Wada T, Wang L, Sasabe H. Amorphous conjugated carbazole trimers for photorefractive materials. Chemistry of Materials 1997;9(12):2798–804.

[9] Sonntag M, Kreger K, Hanft D, Strohriegl P. Novel star-shaped triphenylamine-based molecular glasses and their use in OFETs. Chemistry of Materials 2005;17(11):3031–9.

[10] Zhang Q, Chen J, Wang L. Novel hole-transporting materials based on 1,4-bis(carbazolyl)benzene for organic light-emitting devices. Journal of Materials Chemistry 2004;14:895–900.

[11] Ishikawa W, Noguchi K, Kuwabara Y, Shirota Y. Novel amorphous molecular materials: the starburst molecule 1,3,5-tris[*N*-(4-diphenyl-aminophenyl)phenylamino]benzene. Advanced Materials 1993;5(7):559–61.

[12] Koene BE, Loy DE, Thompson ME. Asymmetric triaryldiamines as thermally stable hole transporting layers for organic light-emitting. Chemistry of Materials 1998;10(8):2235–50.

[13] Loiseau L, Campagna S, Hameurlaine A, Dehaen W. Dendrimers made of porphyrin cores and carbazole chromophores as peripheral units: absorption spectra, luminescence properties, and oxidation behavior. Journal of the American Chemical Society 2005;127(32):11352–63.

[14] Roquet S, Cravino A, Leriche P, Alévêque O, Frère P, Roncali J. Triphenylamine–thienylenevinylene hybrid systems with internal charge transfer as donor materials for heterojunction solar cells. Journal of the American Chemical Society 2006;128(10):3459–66.

[15] Leriche P, Frère P, Cravino A, Alévêque O, Roncali J. Molecular engineering of the internal charge transfer in thiophene–triphenylamine hybrid π-conjugated systems. The Journal of Organic Chemistry 2007;72(22):8332–6.

[16] Wei P, Bi X, Wu Z, Xu Z. Synthesis of triphenylamine-cored dendritic two-photon absorbing chromophores. Organic Letters 2005;7(15):3199–202.

[17] Yoon KR, Ko SO, Lee SM, Lee H. Synthesis and characterization of carbazole derived nonlinear optical dyes. Dyes and Pigments 2007;75:567–73.

[18] Bing YJ, Leung LM, Menglian G. Synthesis of efficient blue and red light emitting phenanthroline derivatives containing both hole and electron transporting properties. Tetrahedron Letters 2004;45:6361–3.

[19] Bacher E, Bayerl M, Rudati P, Reckefuss N, Muller CD, Meerholz K, et al. Synthesis and characterization of photo-cross-linkable hole-conducting polymers. Macromolecules 2005;38(5):1640–7.

[20] Wang S, Yu C, Choi MS, Kim SH. A switching fluorescent photochromic carbazole–spironaphthoxazine copolymer. Dyes and Pigments 2008;77:245–8.

[21] Chen L, Cui Y, Mei X, Qian G, Wang M. Synthesis and characterization of triphenylamino-substituted chromophores for nonlinear optical applications. Dyes and Pigments 2007;72:293–8.

[22] Zhang Q, Ning Z, Tian H. 'Click' synthesis of starburst triphenylamine as potential emitting material. Dyes and Pigments 2009;81:80–4.

[23] Schmitz C, Pösch P, Thelkkat M, Schmidt HW, Montali A, Feldman K, et al. Polymeric light-emitting diodes based on poly(*p*-phenylene ethynylene), poly(triphenyldiamine), and spiroquinoxaline. Advanced Functional Materials 2001;11(1):41–6.

[24] Tomas KRT, Lin JT, Tao YT, Chuen CH. Quinoxalines incorporating triarylamines: potential electroluminescent materials with tunable emission characteristics. Chemistry of Materials 2002;14(6):2796–802.

[25] Karastatiris P, Mikroyannidis JA, Spiliopoulos LK. Synthesis, photophysics, and electroluminescence of new quinoxaline-containing poly(p-phenylenevinylene)s. Macromolecules 2004;37(21):7867–78.

[26] Kulkarni AP, Zhu Y, Jenekhe SA. Quinoxaline-containing polyfluorenes: synthesis, photophysics, and stable blue electroluminescence. Macromolecules 2005;38(5):1553–63.

[27] Huang TH, Whang WT, Shen JY, Wen YS, Lin JT, Ke TH, et al. Dibenzothiophene/oxide and quinoxaline/pyrazine derivatives serving as electron-transport materials. Advanced Functional Materials 2006;16(11):1449–56.

[28] Feng GL, Ji SJ, Lai WY, Huang W. Synthesis and optical properties of starburst carbazoles based on 9-phenylcarbazole core. Synlett 2006:2841–5.

[29] Feng GL, Lai WY, Ji SJ, Huang W. Synthesis of novel star-shaped carbazole-functionalized triazatruxenes. Tetrahedron Letters 2006;47:7089–92.

[30] Miyaura N, Suzuki A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. Chemical Reviews 1995;95(7):2457–83.

[31] Hu NX, Xie S, Popovic ZD, Wong BA, Hor M. Novel high T_g hole-transport molecules based on indolo[3,2-*b*]carbazoles for organic light-emitting devices. Synthetic Metals 2000;111:421–4.

[32] Thomas KRJ, Lin JT, Tao YT, Ko CK. New star-shaped luminescent triarylamines: synthesis, thermal, photophysical, and electroluminescent characteristics. Chemistry of Materials 2002;14(3):1354–61.

[33] Li Y, Ding J, Day M, Tao Y, Lu J, D'iorio M. Synthesis and properties of random and alternating fluorene/carbazole copolymers for use in blue light-emitting devices. Chemistry of Materials 2004;16(11):2165–73.

[34] Zhao Z, Xu X, Jiang Z, Lu P, Yu G, Liu Y. Oligo(2,7-fluorene ethynylene)s with pyrene moieties: synthesis, characterization, photoluminescence, and electroluminescene. Journal of Organic Chemistry 2007;72(22):8345–53.

[35] Janietz S, Bradley DDC, Grell M, Giebeler C, Inbaselatan M, Woo EP. Electrochemical determination of the ionization potential and electron affinity of poly(9,9-dioctylfluorene). Applied Physics Letters 1998;73(17):2453–5.

[36] Pommerehne J, Vestweber H, Guss W, Mahrt RF, Bässler H, Porsch M, et al. Efficient two layer LEDs on a polymer blend basis. Advanced Materials 1995;7(6):551–4.

[37] Yu G, Yin S, Liu Y, Shuai Z, Zhu D. Structures, electronic states, and electroluminescent properties of a zinc(II) 2-(2-hydroxyphenyl)benzothiazolate complex. Journal of the American Chemical Society 2003;125(48):14816–24.

[38] Cui Y, Zhang X, Jenekhe SA. Thiophene-linked polyphenylquinoxaline: a new electron transport conjugated polymer for electroluminescent devices. Macromolecules 1999;32(11):3824–6.

[39] Thelakkat M, Schmidt HW. Synthesis and properties of novel derivatives of 1,3,5-tris(diarylamino) benzenes for electroluminescent devices. Advanced Materials 1998;10(3):219–23.

[40] Zhang XH, Lai WY, Gao ZQ, Wong TC, Lee CS, Kwong HL, et al. Photoluminescence and electroluminescence of pyrazoline monomers and dimmers. Chemical Physics Letters 2000;320(2):77–80.

[41] Tao YT, Balasubramaniam E, Danel A, Tomasik P. Dipyrazolopyridine derivatives as bright blue electroluminescent materials. Applied Physics Letters 2000;77(7):933–5.

[42] Kwong RC, Lamansky S, Thompson ME. Organic light-emitting devices based on phosphorescent hosts and dyes. Advanced Materials 2000;12(15):1134–8.