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Spectral studies of multi-branched fluorescence dyes based on triphenylpyridine core



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HIGHLIGHTS

• New fluorescence dyes based on triphenylpyridine were synthesized.

- Compounds exhibited efficient emission from blue to green with high quantum yields.
- HOMO/LUMO energy levels were obtained by CV and theoretical calculation.
- The effects of solvents on the fluorescence characteristics were investigated.
- All of the compounds possess of suited HOMO ranges (-5.56 to -5.70 eV).

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New framework triphenylpyridine derivatives containing triphenylamine groups were synthesized and the relationship of photoluminescence property and structure were investigated. Quantum chemical calculations were used to obtain optimized ground-state geometry, spatial distributions of the HOMO, LUMO levels of the compounds.



ABSTRACT

A series of novel triphenylpyridine-containing triphenylamine derivatives have been carefully designed and prepared in good yields using the stepwise route reactions. The relationship of photoluminescence property and structure of compounds **9–13** was systematically investigated via UV–vis, fluorescence, thermogravimetric and electrochemical analyzer. The highest occupied molecular orbital and the lowest unoccupied molecular orbital distributions of compounds **9–13** were calculated by density functional theory method. The high fluorescence quantum yields, desirable the highest occupied molecular orbital levels and high thermal stability of compounds **9–13** indicate that the linkage of triphenylpyridine and triphenylamine is an efficient means to enhance hole-transporting ability and fluorescent quantum yield. © 2013 Elsevier B.V. All rights reserved.

Introduction

Organic fluorescent compounds have been extensively investigated for a myriad of potential applications in the biological labels, photovoltaic cells, light emitting diodes, and optical sensors etc.

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[1–12]. Fluorescent characteristic relies largely on molecular structure and assembly. Therefore, it is important to clarify the structure–property relationship of fluorescence because it enable us to design and employ more useful fluorescent reagents in the fields of analytical, biological chemistry and OLEDs in the future.

Triphenylamine molecular possesses a propeller-shaped structure with highly rich electron and it can maintain uninterrupted conjugation between central nitrogen lone pair electrons and the arms. In recent years, it has been widely employed in organic light emitting diodes, organic solar cells or organic field-effect transistors as electron-donating moieties [13–33]. Pyridine has been a key building block in constructing functional materials in view of its outstanding mechanical and dielectric properties [34–39].

Therefore, to afford suitable fluorescent materials [40,41] with higher hole-transporting ability and fluorescent quantum yield for analytical and biological chemistry, herein we introduced triphenylamine units into the 2,4,6-triphenylpyridine framework. As expected, the fluorescence emission color of products can be easily tuned from blue to green by changing the number of triphenylamine moieties and these compounds **9–13** possess higher fluorescence quantum yields (0.30–0.45) except compound **12**. Particularly, these compounds exhibit good the highest occupied molecular orbital (HOMO) levels (–5.56 to –5.70 eV), which is lower than that of the widely-used, hole-transporting material, 4,4-bis(1-naphthylphenylamino)biphenyl (NBP) (–5.50 eV), it might be beneficial for the hole-transport capacity. As a result, these compounds lead to promising applications in functional materials.

Experimental

Chemicals and instruments

All solvents were carefully dried and freshly distilled. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. ¹H and spectra were recorded at 295 K on a Bruker Avance DPX-400 MHz spectrometer using $CDCl_3$ or d_6 -DMSO as solvent and TMS as internal standard. UV-vis absorption spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-4500 spectrofluorometer. HRMS data were measured using microTOF-Q(ESI) instrument. Thermal properties was performed under nitrogen on a SDT 2960 (heating rate of 20 $^{\circ}$ C min⁻¹). Cvclic voltammetry was carried on a Chi 1200 A 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 CH₂Cl₂ solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) $(0.10 \text{ mol } \text{L}^{-1})$ as supporting electrolyte.

4-(Diphenylamino)benzaldehyde (2a)

Phosphorus oxychloride (1.6 mL, 16.8 mmol) was added dropwise to DMF (1.3 mL, 19.5 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. Triphenylamine (3.3 g, 13.3 mmol) was added and the reaction mixture was stirred at 100 °C for 6 h. Then, the mixture was cooled to room temperature, poured into ice water and carefully neutralized to pH 7 with 5% NaOH aqueous solution. The solution was extracted with dichloromethane (3×150 mL). Then, the organic phase was washed with water (2×100 mL) and dried over anhydrous MgSO₄. After filtration, the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane, 3/1, v/v) to produce white solid.

Compound **2a**: yield 82%, white ¹H NMR (400 MHz, CDCl₃): 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).

4,4'-Diformyl triphenylamine (2b)

Phosphorus oxychloride (9.23 mL, 0.1 mol) was added dropwise to a stirred (7.74 mL, 0.1 mol) of DMF at 0 °C. The mixture was stirred at 0 °C for 1 h and then stirred at room temperature for another 1 h. After the loading of (10.0 g, 0.04 mol) of triphenylamine dissolved in chloroform, the mixture was stirred at 100 °C for 48 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with 5% NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at vacuum. The residue was chromatographed on a silica gel column (silica gel, hexane/dichloromethane, 3/1, v/v) to produce of yellowish solid.

Compound **2b**: yield 70%, yellow ¹H NMR (400 MHz, CDCl₃): δ 9.89 (s, 2H), 7.84 (d, *J* = 8.4 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.18–7.20 (m, 6H).

Tris-(4-formyl-phenyl)amine (2c)

Phosphorus oxychloride (9.23 mL, 0.1 mol) was added dropwise to a stirred (7.74 mL, 1.0 mol) of DMF at 0 °C. The mixture was stirred at 0 °C for 1 h and additionally stirred at room temperature for 1 h. After the addition of (6.0 g, 0.02 mol) of **2b** in chloroform, the mixture was stirred at 100 °C for 48 h. After cooling, the solution was poured into water. The resulting mixture was neutralized to pH 7 with 5% NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at vacuum. The residue was chromatographed on a silica gel column (silica gel, hexane/dichloromethane, 2/1, v/v) to produce yellowish solid.

Compound **2c**: yield 20%, yellow ¹H NMR (300 MHz, CDCl₃): δ 9.95 (s, 3H), 7.86 (d, *J* = 8.7 Hz, 6H), 7.27 (d, *J* = 8.1 Hz, 6H).

1,3,5-Trip-tolylpentane-1,5-dione (5)

A mixture of *p*-tolualdehyde **3** (1.8 g, 15 mmol), 4-methylacetophenone **4** (4.3 g, 32 mmol) and powder NaOH (2.4 g, 60 mmol) were crashed together with a pestle and mortar for 2 h and then recrystallized with ethanol to give white needle crystal. Yield: 4.73 g, 85%.

2,6-Diphenyl-4-p-tolyl-pyridine (6d)

1,3,5-trip-tolylpentane-1,5-dione (**5d**) (3.7 g, 10 mmol) was added to a stirred solution of ammonium acetate (8 g, excess) in ethanol (100 mL). The reaction mixture was heated at refluxing for 10 h. Upon cooling to room temperature; a precipitate was filtered, washed with water three times and dried to afford the product. It was purified by flash column chromatography on silica. Elution with petroleum/ethyl acetate (8:1) gave a white solid **6d**. Yield: 2.8 g, 75%. Mp: 181–183 °C.IR (cm⁻¹): 3027, 2962, 2919, 2858, 1600, 1543, 1389, 1184, 1114, 1018, and 809. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.81 (s, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.30 (d, 6H), 2.42 (s, 9H).

Phosphonium salt (8)

Phosphonium salt **8** prepared via free radical bromination of (6a-c) with NBS (Fig. 1) and was reacted with triethylphosphite to yield phosphoniumsalt **8a–c** (without isolation for further reaction).



Fig. 1. Synthetic routines for compound 2 and 8a. Reagents and conditions: (a) POCl₃, DMF, 0 °C, CHCl₃, 100 °C; (b) NaOH (c) NH₄OAc, EtOH, 80 °C; (d) NBS, CCl₄, 80 °C; (e) PO(OEt)₃, 185 °C.



Fig. 2. Synthetic routines of 11. Reagents and conditions: (f) cat. Pd(PPh₃)₄, 2 mol L⁻¹ K₂CO₃, toluene, 90 °C.

4-(2,6-Diphenypyridin-4-yl)-N,N-diphenylaniline (9)

The compound **9** was synthesized through the same procedure as that of compound **6** described above using **2a** and **4** as starting material.

Yield 90%, yellow solid, m. p. 165.0–166.1 °C, ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 4.0 Hz, 4H), 7.87 (s, 2H), 7.64 (d, *J* = 4.0 Hz, 2H), 7.54–7.50 (m, 4H), 7.47–7.43 (m, 2H), 7.33–7.29 (m, 4H), 7.20–7.16 (m, 6H), 7.11–7.05 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 116.51, 123.18, 123.57, 124.94, 127.16, 127.92, 128.72, 129.01, 129.48, 132.11, 139.75, 147.37, 148.88, 149.56, 157.47 ppm.

HRMS (ESI) m/z: calc. for $C_{35}H_{26}N_2$, $(M + H)^+$: 475.2174, Found: 475.2131.

4'-(2,6-Diphenypyridin-4-yl)-N,N-diphenylbiphenyl-4-amine (11)

Under a nitrogen atmosphere, a mixture of compound **6d** (1.0 mmol), Pd(PPh₃)₄ catalyst (0.04 mmol) and the corresponding triphenylamine boronic acid **10** was stirred in dry toluene (15 mL). Then, 2 mol L⁻¹ K₂CO₃ (aq) solution (2 mL)was added via syringe. The reaction mixture was refluxed for 72 h. After cooling, the product was extracted with DCM, washed with water, dried over MgSO₄, filtered, concentrated and further purified by column chromatography (silica gel, hexane/dichloromethane, 10/1, v/v), to afford pure compounds **11**.

Yield 85%, white solid, m. p. 213.1–214.6 °C, ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 4.0 Hz, 4H), 7.94 (s, 2H), 7.83 (d, *J* = 4.0 Hz, 2H), 7.74 (d, *J* = 4.0 Hz, 2H), 7.56–7.46 (m, 8H), 7.30 (d, *J* = 4.0 Hz, 4H),



Fig. 3. Synthetic routines of 12 and 13. Reagents and conditions: (g) THF, 60 °C.

7.17 (s, 6H), 7.07 (d, J = 4 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 123.16, 123.65, 124.62, 127.20, 127.23, 127.54, 127.73, 128.73, 129.12, 129.34, 133.85, 137.11, 139.42, 141.44, 147.57, 147.68, 149.84, 157.49 ppm.

HRMS (ESI) m/z: calc. for $C_{41}H_{30}N_2$, $(M + H)^+$: 551.2487, Found: 551.2443.

General procedure for the synthesis of compounds (12 and 13)

Under a nitrogen atmosphere, a mixture of compounds **8a-c** and compound **2a-c** (2.0 mmol) in dry THF (5 mL) was added dropwise and the mixture were refluxed at 60 °C for 2 h. The mixture was cooled and quenched with EtOH. The solvents were then removed



Fig. 4. The absorption spectra of compounds 9-13 (1 \times 10⁻⁶ mol L⁻¹ in CH₂Cl₂).



Fig. 5. PL emission spectra of compounds **9–13** (1×10^{-6} mol L⁻¹ in THF).

Table 1Optical properties of the compounds 9–13.

Compound	Abs. (nm)		em (nm)		Φ^{a}
	CH ₂ Cl ₂	Toluene	THF	DMF	
9	354	415	445	470	0.42
11	353	428	463	501	0.45
12a	412	455	491	520	0.35
12b	387	463	497	532	0.30
12c	403	468	502	540	0.27
13a	395	448	474	504	0.32
13b	391	452	484	509	0.33

^a The fluorescence quantum yields (Φ) were measured in THF using quinine sulfate (Φ = 0.55) as standard [46].

under vacuum, the solid was dissolved in CH_2Cl_2 , washed in distilled H_2O , dried over MgSO₄ and the solvent was removed. The residue was chromatographed on a silica gel column (silica gel, hexane/dichloromethane, 4/1, v/v) to produce compound **12** and **13**.

(E)-4-(4-(2,6-diphenylpyridin-4-yl)styryl)-N,N-diphenylaniline (12a) Yield 72%, yellow solid, m. p. 182.2–183.5 °C, ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, J = 4.0 Hz, 4H), 7.92 (s, 2H), 7.76 (d, J = 4.0 Hz, 2H), 7.65 (d, J = 4.0 Hz, 2H), 7.55–7.51 (m, 4H), 7.48– 7.42 (m, 4H), 7.29 (d, J = 4.0 Hz, 4H), 7.17–7.03 (m, 10H) ppm.
¹³C NMR (100 MHz, CDCl₃): δ 116.72, 119.36, 123.17, 123.39,



Fig. 6. The emission spectra of compound 13a in different solvents $(1\times 10^{-7}\,\text{-mol}\,L^{-1})$ as sample.

124.62, 125.10, 126.02, 126.31, 126.95, 127.15, 127.41, 127.51, 128.70, 129.03, 129.23, 129.32, 129.72, 137.53, 138.52, 139.63, 147.48, 147.68, 149.61, 157.55 ppm.

HRMS (ESI) m/z: calc. for $C_{43}H_{32}N_2$, (M + H)+: 577.2644, Found: 577.2598.

4-(4-(2,6-Diphenylpyridin-4-yl)styryl)-N-(4-(4-(2,6-diphenylpyridin-4-yl)styrl)phenyl)-N-phenylaniline (**12b**)

Yield 60%, yellow solid, m. p. 139.0–141.6 °C, ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 4.0 Hz, 7H), 7.60–7.58 (m, 4H), 7.40–7.32 (m, 22H), 7.16–7.13 (m, 4H), 5.96 (s, 4H), 5.53 (s, 8H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 116.72, 123.66, 123.95, 125.01, 126.38, 127.02, 127.18, 127.45, 127.64, 128.74, 129.07, 129.15, 129.48, 131.67, 137.64, 138.46, 139.66, 147.19, 147.28, 149.59, 157.58 ppm.

HRMS (ESI) m/z: calc. for $C_{68}H_{49}N_3$, (M + H)+: 908.4005, Found: 908.3998.

Tris(4-(4-(2,6-diphenylpyridin-4-yl)styryl)phenyl)amine (12c)

Yield 34%, yellow solid, m. p. 158.1–160.5 °C, ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 4.0 Hz, 12H), 7.92 (s, 6H), 7.78 (d, *J* = 4.0 Hz, 5H), 7.67 (d, *J* = 4.0 Hz, 5H), 7.55–7.45 (m, 26H), 7.23–7.10 (m, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 116.72, 124.36, 126.63, 127.05, 127.17, 127.47, 127.72, 128.74, 129.08, 132.12, 137.72, 138.38, 139.64, 146.88, 149.56, 157.59 ppm.

HRMS (ESI) m/z: calc. for $C_{93}H_{66}N_4$, $(M + H)^{\ast}{:}$ 1240.5399, Found: 1240.5087.

4,4'-(1E,1'E)-2,2'-(4,4'-(4-phenylpyridine-2,6-diyl)bis(4,1phenylene))bis(ethene-2,1-divl)bis(N,N-diphenylaniline) (**13a**)

Yield 68%, yellow solid, m. p. 125.4–126.7 °C, ¹H NMR (400 MHz, CDCl₃): δ 8.27–8.21 (m, 3H), 7.91–7.85 (m, 2H), 7.78– 7.63 (m, 6H) 7.57–7.42 (m, 6H), 7.36–7.27 (m, 6H), 7.19–6.98 (m, 24H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 116.78, 119.37, 122.66, 123.09, 123.52, 124.17, 124.21, 124.56, 125.10, 126.31, 126.59, 126.64, 127.20, 127.37, 127.47, 127.72, 128.77, 129.11, 129.19, 129.23, 129.30, 129.73, 131.43, 138.35, 138.42, 139.16, 147.51, 147.54, 150.14, 157.01 ppm.

HRMS (ESI) m/z: calc. for $C_{63}H_{47}N_3$, (M + H)^+: 847.3882, Found: 847.3847.

4,4',4"-(1E,1'E,1"E)-2,2',2"-(4,4',4"-(pyridine-2,4,6-triyl)tris(benzene-4,1-diyl)tris(ethene-2,1-diyl)tris(N,N-diphenylaniline) (13b)

Yield 29%, yellow solid, m. p. 142.1–144.6 °C, ¹H NMR (400 MHz, d_6 -CDCl₃): δ 8.22 (d, 4H, J = 4.0 Hz), 7.89 (d, 2H,

9-13.

Table 2
Thermal, and electrochemical properties of the compounds

Compound	Band gap ^a	E _{HOMO} / E _{LUMO} (eV) ^a	$E_{\rm g}$ (eV) ^b	E ^{ox} onset ^c (V)	$\frac{E_{\rm HOMO}}{E_{\rm LUMO}}^{\rm d}$ (eV)	$T_{\rm g}/T_{\rm d}^{\rm e}$ (°C)
9	3.81	-5.11/ -1.30	2.95	1.23	-5.67/ -2.72	68/ 188
11	3.59	-5.03/ -1.44	3.02	1.26	-5.66/ -2.64	62/ 170
12a	3.21	-4.92/ -1.71	2.61	1.30	-5.70/ -3.09	95/ 208
12b	3.05	-4.92/ -1.87	2.76	1.16	-5.56/	80/ 230
12c	3.05	-4.78/	2.64	1.28	-5.68/	89/ 226
13a	3.19	-4.79/	2.70	1.34	-5.74/	110/
13b	3.00	-4.93/ -1.93	2.74	1.16	-5.56/ -2.82	127/ 204

^a DFT/B3LYP calculated values.

^b Optical energy gaps calculated from the edge of the electronic absorption band. ^c Oxidation potential in CHCl₃ (10^{-3} mol L⁻¹) containing 0.1 mol L⁻¹ (n-C₄H₉)₄₋ NPF₆ 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 N₂ at a heating rate of 20 °C min⁻¹.

J = 4.0 Hz), 7.76 (d, 2H, *J* = 4.0 Hz), 7.65 (d, 6H, *J* = 4.0 Hz), 7.52–7.27 (m, 10H), 7.14–7.01 (m, 38H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 122.82, 123.11, 123.20, 123.44, 123.54, 124.08, 124.23, 124.58, 124.65, 126.67, 126.98, 127.40, 127.51, 127.56, 128.27, 128.77, 129.26, 129.33, 131.45, 138.41, 147.52, 147.56 ppm.

HRMS (ESI) m/z: calc. for $C_{83}H_{62}N_4$, $(M + Na)^+$: 1137.4872, Found: 1137.4844.

Results and discussion

Compounds **2**, **6** and **9** were synthesized according to the literature methods [22,35] (Fig. 1). For products **11**, **12** and **13**, the triphenylamine was introduced via a Pd(0) catalyzed Suzuki C–C coupling reaction or Wittig–Horner condensation reactions [41] (Figs. 2 and 3). New compounds were characterized by MS spectrometry, ¹H NMR spectroscopy.

Optical properties

The UV-vis absorption and fluorescence properties of compounds **9–13** in CH₂Cl₂ and THF are shown in Fig. 4 and 5. Their comprehensive photophysical characteristics 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 **9–13** are located in the range of 355–410 nm, which is supposed to be ascribed to the π - π * transition of the conjugated molecular backbone.

The maximum absorption peak of the alkenyl bridged oligomer **12a** was red shifted by 65 nm with respect to the Compounds **9** and **11**. The π - π energy gap (ΔE) of these oligomers was calculated from the UV-vis absorption maximum [42]. It was obvious that the ΔE value of **9–13** could be reduced by the introduction of alkenyl spacers at the backbone.

Fig. 5 shows the fluorescence emission spectra of compounds **9–13** in the excitation of 350 nm. These compounds indicate a blue to green fluorescence emission with the maximum emission peaks varying from 445 to 502 nm in THF solutions. With increasing triphenylpyridine or triphenylamine moieties, the fluorescence emission peaks for **9–13** are gradually red shifted. Compound **12c** exhibits strong green fluorescence maxima at about 502 nm due to possess maxima conjugation length.



Fig. 7. Cyclic voltammogram of compound $13c~(1\times 10^{-3}\,mol\,L^{-1})$ as sample, in 0.1 mol L^{-1} Bu4NPF6-CHCl3, scan rate 100 mV/s.



Fig. 8. Optimized ground-state geometry of compounds **13a** with B3LYP/6-31G* in gas phase.

Compounds **9** and **11** have similar fluorescence spectra because these compounds possess a similar structure. Especially, the similar shape, position and one emission peak near 450 nm were observed for these molecules.

The further examination in the different emission behavior of these compounds found out that these compounds showed a red shift with increasing solvent polarity (Fig. 6) [43]. These results indicate that these compounds are more polar in the excited state than in the ground state [44] and an increase in the polarity of the solvent will lower the energy level of the charge transfer excited state [45].

The fluorescence quantum yields (Φ) were measured in the THF solution using quinine sulfate (Φ = 0.55) as a standard (Table 1) [46]. The emission efficiency in dilute solution largely depends on the molecular structure. The fluorescence quantum yields of the compounds are in the range of 0.27–0.45. The Φ value of 0.42 and 0.45 was observed for **9** and **11**, which was higher than that of compounds **12** and **13**. They show that the introduction of alkenyl bridge and multi-branched structure reduce coplanarity degree of compounds **12** and **13**, which might lead to concentration quenching effects [47]. Moreover, this difference of the quantum yields may appear during the process of the exciton migration [48], or result from the change of the molecular size [49].

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. 62–127 °C (Table 2). The experiment results revealed that the thermal stability of these compounds seemed to be encouraging. Thermal decomposition



Fig. 9. Calculated spatial distributions of the HOMO, LUMO levels of compound 13a as sample.

temperatures for **9–13** were observed at 188, 170, 208, 230, 226, 226 and 204 °C, respectively, which is due to the conjugation length and asymmetric nature of the molecules.

Electrochemical properties

The electrochemical properties of compounds 9-13 are explored by the cyclic voltammetry in the CHCl₃ solutions in the tetrabutylammonium hexafluorophosphate presence of $(0.10 \text{ mol } L^{-1})$ as the supporting electrolyte (Table 2). All of compounds 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 a range of -5.56 to -5.70 eV [50,51]. Since the HOMO energy level is close to that of the most widely used hole-transport material 4,4'-bis(1-naphthylphenylamino)biphenyl (NBP) (-5.20 eV, -2.4 eV), it might be beneficial for the hole-transport capacity [51]. Similarly, the optical edge was utilized to deduce the band gap and the lowest unoccupied molecular orbital (LUMO) energies. As expected, these compounds are of lower LUMO (-2.61 to -2.74 eV) energies and smaller band gaps compared with other triphenylamine derivatives [52]. Their LUMO levels represent a small barrier for the electron injection from a commonly used cathode such as barium, which has a work function of -2.2 eV [53]. Therefore, these compounds might be very useful as hole-transporting and electron-transporting materials in applications for OLEDs [53].

Theoretical calculations

The electronic configurations were further examined using the theoretical models implanted in the Gaussian 03 program [54]. 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 9-13. Due to the presence of the electron-rich amine moieties and an increase in the conjugation lengths, all of these compounds in Table 2 possess a high HOMO energy level (-4.92 to -5.11 eV) (Figs. 8 and 9) [52]. The low LUMO energy of these compounds (-1.30 to)-1.93 eV) 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. The higher HOMO/LUMO energy levels than those corresponding estimations from the experimental data may be related to various effects from conformation and solvents, which have not been taken into account here. Moreover, the electrochemistry is complicated owing to the reversibility of one of the redox process and the accuracy of the Eg value is relatively limited [55].

Conclusions

In summary, a series of new framework fluorescence dyes based on triphenylpyridine derivatives containing triphenylamine groups have been prepared by a stepwise route in good yields. The optical properties clearly indicate that the fluorescent emission properties of these compounds rely largely on the molecular structure. As expected, the optical band gaps decrease considerably as the number of triphenylamine moieties introduced into triphenylpyridine framework increases. Moreover, compounds exhibited high fluorescence quantum yields, high thermal stability and excellent luminescence emission from blue to green. The DFT calculations establish that they all possess a high HOMO energy level (-4.92 to -5.11 eV) due to the presence of the electron-rich amine moieties and increased conjugation lengths, giving rise to more balanced charge-transport characteristics, which have promising potential for application in OLEDs as a multifunctional material.

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