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ARTICLE

Violet-blue- or pure-blue-emitting triphenylamine derivatives: synthesis and properties

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Abstract: We report the synthesis and optoelectronic properties of a series of nine triphenylamine derivatives. They were synthesized by Suzuki cross-coupling reactions and characterized by elemental analysis, nuclear magnetic resonance, ultraviolet visible absorption spectra, fluorescence spectra, and cyclic voltammetry. All compounds exhibit reversibly electrochemical behavior. In solid state, compounds **5** and **9** emit near violet blue and compounds **1**, **2**, **4**, **6**, **7**, and **8** emit deep blue or pure blue and compound **3** emits green. Of all of these compounds, compounds **1**, **3**, **4**, and **8** exhibit high fluorescence quantum yields (44%–68%) with the best coplanarity. Compared with them, compounds **5** and **9** have the lowest fluorescence quantum yields due to the least coplanarity. With the similarity in structure with those reported in literature, these compounds can be potentially useful for blue-emitting, host, and up-converting materials.

Key words: triphenylamine, violet blue, blue-emitting, quantum yield, electrochemistry.

Résumé : On présente la synthèse et les propriétés optoélectroniques d'une série de neuf dérivés de la triphénylamine. Ces dérivés ont été synthétisés par des réactions de couplage de Suzuki et caractérisés en se basant sur l'analyse élémentaire, la résonance magnétique nucléaire, les spectres d'absorption ultraviolet-visible, les spectres de fluorescence et la voltammétrie cyclique. Tous les composés présentent un comportement électrochimique réversible. À l'état solide, les composés **5** et **9** émettent dans le bleu tirant sur le violet, les composés **1**, **2**, **4**, **6**, **7** et **8** émettent dans le bleu foncé ou le bleu pur, et le composé **3** émet dans le vert. Les composés **1**, **3**, **4** et **8** présentent un rendement quantique de fluorescence élevé (44%–68%) et la meilleure coplanarité. Comparativement, les composés **5** et **9**, qui possèdent le moins de coplanarité, donnent le rendement quantique de fluorescence le plus faible. En raison de la similarité entre leur structure et celle des composés décrits dans la littérature, ces composés pourraient être utiles à titre de matériaux émettant dans le bleu, de matériaux hôtes et de matériaux convertisseurs élévateurs de fréquence. [Traduit par la Rédaction]

Mots-clés : triphénylamine, bleu-violet, émettant dans le bleu, rendement quantique, électrochimie.

Introduction

Organic light-emitting diodes (OLEDs) have been widely recognized as the next-generation technology for flat panel displays and white lighting.[1–5] In recent years, there has been considerable interest in developing organic electroluminescence devices with high luminance for white lighting, with high efficiency and stability for long-driving lifetime displays.[6–12] Especially, blue electroluminescence materials attracted much attention.[6,7,13–17] This is because on one hand, for full color applications, red, green, and blue (RGB) emission are required.[18] On the other hand, an efficient blue or violet-blue emission can be down-converted to other low-energy colors, like green and red. However, the performance of blue material was generally low compared with its red and green counterparts[19] because it is more difficult to produce a blue emission due to its intrinsic characteristic of having a wide band gap irrespective of the type of materials.

In addition, violet-blue- and blue-emitting materials have been used for hosts to other blue/green/red-emitting fluorescent and phosphorescent materials based on the "overlap" principle.[20–24] Although there are a number of efficient blue dyes that have been developed in the past several years,[25–31] efficient violet-blue- or blue-emitting materials are still a bottleneck to the development of OLEDs, which encourages us to do research in seeking good blue-emitting materials.

Triarylamine and its derivatives have often been used as the building blocks for efficient hole-transport, blue-emitting, and host materials,[32–41] e.g., triphenylamine itself has a high triplet energy of 3.04 eV and good hole-transporting ability.[42] Triphenylamine/fluorene hybrid and triphenylamine/oxadiazole derivative are good host materials.[43,44]

In this paper, we report the synthesis and properties of a series of triphenylamine derivatives. Of the nine compounds synthesized, eight compounds emit violet-blue or pure-blue light. With similar structures as those reported in literature, we are sure they can be potentially useful for blue-emitting, up-converting, or host materials.

Experimental

Chemicals and instruments

All chemicals were used as purchased from commercial sources. All solvents were carefully dried according to common laboratory techniques. Melting point was recorded on an X-4 microscopic melting point instrument. ^{1}H NMR data were collected on a Bruker Avance DRX-400 NMR spectrometer in $CDCl_3$. Absorption spectra were recorded on a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer. Fluorescent spectra were recorded on a Hitachi F-4500 spectrophotometer. Cyclic voltammograms were carried out in 0.10 mol L^{-1} n-Bu_4NClO_4 dissolved in freshly dried

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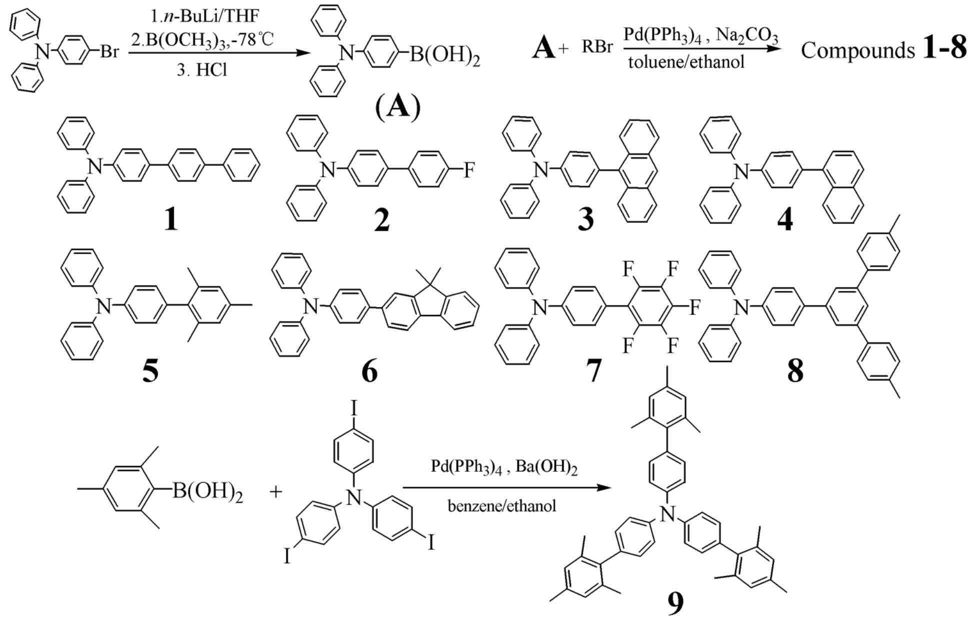
Scheme 1. Synthetic routes of compounds **1–9**.



dichloromethane on an Autolab Potentiostat 30. All potentials were quoted against an $F^{+}{}_{c}/F^{-}{}_{c}$ couple, unless otherwise stated, whose half-wave potential is 0.55 ± 0.01 V against the above Ag/AgCl reference electrode. All experimental manipulations and data collections were performed at room temperature, unless otherwise stated.

Synthesis

The chemical structure and the synthetic procedure for the target compounds **1–9** are illustrated in Scheme 1. Suzuki coupling reactions were used as a key technique to construct the intermediates and the target compounds. References are listed for the intermediates.

Synthesis of 4-(N,N-diphenylamino)-4′-phenyl-1,1′-biphenyl (1)

4-Bromobiphenyl (0.48 g, 2.08 mmol), 4-(*N*,*N*-diphenylamino) benzeneboronic acid[45] (0.5 g, 1.74 mmol), Pd $(PPh_3)_4$ (0.06 g, 0.5 mmol), aqueous Na_2CO_3 (2.0 mol L^{-1}, 15 mL), toluene (30 mL), and ethanol (6 mL) were mixed in a three-necked round-bottom flask (100 mL). The mixture was degassed and refluxed for 24 h under a nitrogen atmosphere. Upon completion, the organic phase was separated and extracted several times with toluene and then evaporated under reduced pressure. The pure product was obtained as a white acicular crystal by column chromatography (silica gel: 200–400 mesh, petroleum ether – dichloromethane = 10:1) and crystallized from ethanol; yield 75.64%, mp 211–212 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.66–7.71 (m, 4H), 7.63–7.6 (t, 2H), 7.51–7.53 (d, 2H, *J* = 8.4 Hz), 7.44–7.48 (t, 2H), 7.34–7.37 (t, 1H), 7.27–7.30 (t, 4H), 7.16 (d, 4H, *J* = 2.4 Hz), 7.14 (d, 2H, *J* = 1.2 Hz), 7.02–7.06 (t, 2H). Anal. calcd. for $C_{30}H_{23}N$: C 90.68, H 5.79, N 3.53; found: C 90.29, H 5.58, N 3.62.

Synthesis of 4-(N,N-diphenylamino)-1-(4-fluorinephenyl)benzene (2)

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 84.43%, mp 94–95 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.57 (d, 2H, *J* = 7.2 Hz), 7.45–7.47 (d, 2H, *J* = 8.8 Hz), 7.39–7.43 (t, 2H), 7.25–7.31 (m, 4H), 7.11–7.14 (d, 6H), 7.99–7.04 (m, 2H). Anal. calcd. for $C_{24}H_{18}NF$: C 84.96, H 5.31, N 4.13; found: C 85.30, H 5.39, N 4.21.

Synthesis of 9-(4′-(N,N-diphenylamino)phenyl)anthracene (3)

The synthetic and purification procedure is similar to that of compound **1** and gives a blue acicular crystal; yield 42.47%, mp 188–190 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.424 (s, 5H), 7.99–8.01 (m, 9H), 7.44–7.47 (m, 9H). Anal. calcd. for $C_{32}H_{23}N$: C 91.92, H 5.46, N 3.33; found: C 90.76, H 5.43, N 3.34.

Synthesis of 1-(4′-(N,N-diphenylamino)phenyl)naphthalene (4)

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 61.38%, mp 138–140 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 7.84–7.91 (m, 3H), 7.72–7.75 (d, 1H, *J* = 8.8 Hz), 7.60–7.62 (d, 2H, *J* = 8.8 Hz), 7.46–7.50 (m, 2H), 7.26–7.31 (t, 4H, J = 8.0 Hz), 7.15–7.20 (t, 6H, *J* = 10 Hz), 7.03–7.07 (t, 2H, *J* = 7.2 Hz). Anal. calcd. for $C_{28}H_{21}N$: C 90.57, H 5.66, N 3.81; found: C 90.61, H 5.23, N 3.81.

Synthesis of 4′-(N,N-diphenylamino)-1-phenyl-2,4,6-trimethylbenzene (5)

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 68.18%, mp 113–115 °C. ^1H NMR (400 MHz, $CDCl_3$), δ: 7.25~7.29 (m, 4H), 7.13~7.15 (m, 6H), 7.00~7.04 (m, 4H), 6.95 (s, 2H), 2.33 (s, 3H), 2.07 (s, 6H). Anal. calcd. for $C_{27}H_{25}N$: C 89.26, H 6.89, N 3.86; found: C 88.79, H 7.79, N 3.81.

Synthesis of 9,9-dimethyl-2-(4′-(N,N-diphenylamino)phenyl)fluorine (6)

Synthesis of 2-bromio-9,9-dimethylfluorene[46]

Yield 91.25%; mp 56–57 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67–7.69 (t, 1H), 7.56–7.58 (s, 1H), 7.55–7.56 (d, 1H, *J* = 4.4 Hz), 7.46 (d, 1H, *J* = 2.0 Hz), 7.40–7.42 (m, 1H), 7.31–7.34 (m, 2H), 1.48 (s, 6H).

Synthesis of 6

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 86.58%, mp 174–175 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.73–7.77 (t, 2H, *J* = 8.0 Hz), 7.63 (s, 1H), 7.54–7.56 (d, 3H, *J* = 8.8 Hz), 7.44–7.46 (d, 1H, *J* = 8.0 Hz), 7.26–7.35 (m, 6H), 7.14–7.18 (t, 6H, *J* = 5.2 Hz), 7.02–7.06 (t, 2H, *J* = 7.6 Hz), 1.53 (s, 6H). Anal. calcd. for $C_{32}H_{27}N$: C 90.35, H 6.35, N 3.29; found: C 90.27, H 6.31, N 2.97.

Synthesis of 6-(4′-(N,N-diphenylamino)phenyl)-1,2,3,4,5-pentafluorine benzene (7)

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 82.0%, mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.32 (m, 6H), 7.16–7.17 (d, 4H, *J* = 7.6 Hz), 7.07–7.13 (m, 4H). Anal. calcd. for $C_{24}H_{14}NF$: C 70.07, H 3.41, N 3.41; found: C 70.38, H 2.86, N 3.37.

Synthesis of 3,5-di(p-methylphenyl)-4′-N,N-diphenylamio-1-phenyl benzene (8)

The synthetic and purification procedure is similar to that of compound **1** and gives a white acicular crystal; yield 41.32%, mp 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 3H), 7.56–7.61 (m, 6H), 7.26–7.30 (t, 8H), 7.15–7.06 (t, 6H), 7.03–7.06 (t, 2H), 2.42 (s, 6H). Anal. calcd. for $C_{38}H_{31}N$: C 91.02, H 6.19, N 2.79; found: C 89.22, H 5.78, N 2.65.

Synthesis of 4,4′,4″-trimesityltriphenylamine (9)

Tri(4-iodophenyl)amine (1.0 g, 1.61 mmol), 2,4,6-trimethylbenzeneboronic acid[47] (1.06 g,6.44 mmol), benzene (50 mL), and ethanol (10 mL) were mixed in a three-necked round-bottom flask (100 mL) under a nitrogen atmospherefor 0.5 h. $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) and $Ba(OH)_2$ saturated solution (3.05 g, 9.66 mmol) were added into the above solution and stirred. The mixture was refluxed for 40 h under a nitrogen atmosphere and then cooled to room temperature and much precipitate was filtered off and diluted with saturated aqueous NH_4Cl solution. Then the solution was extracted with dichloromethane. The organic portions were combined and evaporated under reduced pressure. The pure product was obtained as a white acicular crystal by column chromatography (silica gel: 200–400 mesh, petroleum ether – dichloromethane = 8:1) and crystallized from *n*-hexane; yield 81.77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20–7.23 (d, 2H, *J* = 8 Hz), 7.04–7.06 (d, 2H, *J* = 8 Hz), 6.96 (s, 2H), 2.28 (s, 3H), 2.10 (s, 6H). Anal. calcd. for $C_{45}H_{45}N$: C 90.15, H 7.51, N 2.34; found: C 89.89, H 7.62, N 2.04.

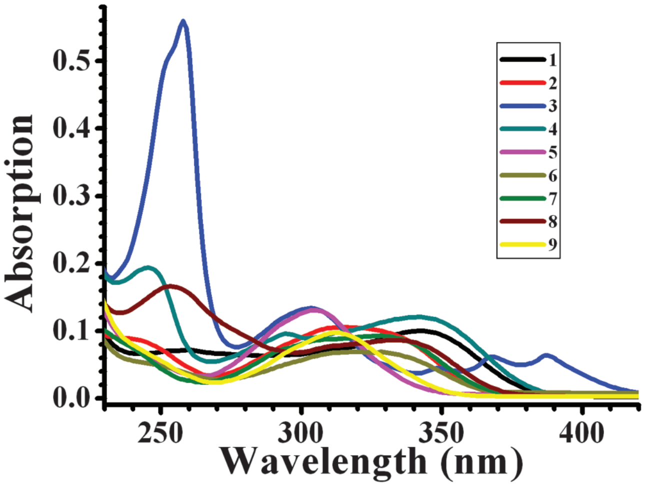
Results and discussion

Absorption and emission spectra

The UV-Vis absorption spectra of compound **1–9** in CH_2Cl_2 solution at room temperature are given in Fig. 1. Other photophysical data are listed in Table 1. All compounds have characteristic strong absorptions at the high-energy 240–280 nm region due to the spin-allowed π–π* transition. The weaker absorption at the lower energy 285–380 nm region corresponds to the forbidden *n*–π* absorption localized at the nitrogen atoms. It should be noted that the absorption of **3** has fine structures in the 340–400 nm region. This will be explained by consulting its emission in the next paragraph. The energy gap, HOMO (highest occupied molecular orbital), and LUMO (lowest unoccupied molecular orbital) can be estimated based on the lowest energy absorption edge of the UV absorption spectrum and electrochemical data (Table 1).

In both CH_2Cl_2 and solid state (see Figs. 2 and 3), the emission of **5** and **9** is violet blue. In CH_2Cl_2, the emission of **2**, **6**, and **8** is deep blue and that of **1**, **4**, and **7** is pure blue. In solid state, the emission is bathochromically shifted compared with that in CH_2Cl_2. Again, it should be noted that the emission of **3** is much different from the others. This is a rather complicated phenomenon. A simple 3D-chemdraw can give us a deeper look to detect the reason (Fig. 4). From Fig. 4, it can be concluded that the mesityl group in **5** and the anthracene group in **3** are in a poorer coplanarity than the biphenyl group in **1**. Poorer coplanarity results in a hypsochromic shift as proven for in **5**. However, in **3**, the emission is greatly bathochromically shifted. This may be caused by an excimer emission. In **3**, both anthracene and the 9-phenyl carbazole group are chromophores; poorer coplanarity may result in an intramolecular excimer, i.e., electrons transit from the excited state of anthracene to the ground state of 9-phenyl carbazole, resulting in a red-shifted excimer emission or vice versa. However, this intramolecular excimer was excluded by Fig. 5, which is the emission of **3** in different concentrations. With the increase in concentration, the 495 nm emission increases, while the 400 nm emission decreases. This is strong evidence that the 495 nm emission is caused by an intermolecular excimer emission. Structurally, the anthracene group with a large conjugative π-system in **3** can easily cause face–face intermolecular interaction in favor of excimer emission.

Fig. 1. UV-Vis absorption spectra of **1–9** in dichloromethane at room temperature.



From the π–π* transition and *n*–π* transition of <380 nm, the short stokes shift, and because of the similarity of the chemical structures of the molecules reported here with those already reported for fluorescent molecules,[39,42,43] we can definitely exclude the possibility of phosphorescence emission of these molecules.

The quantum yield

The quantum yield was determined by excitation at 313 nm in CH_2Cl_2 and using quinine sulfate as the standard.[48] The results coincide with the trend in emission spectra, i.e., compounds **5** and **9** exhibit the least quantum yield with the least coplanarity and compounds **1**, **4**, and **8** have the highest quantum yield with the best coplanarity. As for **3**, the value is also high; this is because, first, the green emission is the most sensitive region to naked eye and, second, the excimer emission itself is of special meaning.

Electrochemical characterization

By cyclic voltammetry, not only the energy levels but also the electrochemical stability can be roughly determined. "Roughly" means that the real energy levels may only be determined in thin film state on the layered OLED device. The stability of an OLED device is a very complicated matter defined not only by the stability of the materials but also by other chemical and physical factors. Figure 6 outlines the cyclic voltammetric curves of all nine compounds. It was recorded with a glassy-carbon electrode in CH_2Cl_2 solutions containing 0.001 mol L^{-1} of the compounds and 0.10 mol L^{-1} n-Bu_4NClO_4 against Ag/AgCl using ferrocene as the internal standard. All compounds exhibit reversible electrochemical behavior with oxidation potentials of around 1–1.2 V.

According to the literature,[49,50] the HOMO energy level can be estimated from the onset potentials (E_{ox} (onset)) through the following equation: $E_{HOMO} = -(4.8 + E_{ref} + E_{ox}\text{ (onset)})$ eV, where E_{ref} is the potential of the ferrocene reference. The energy levels of LUMO and the HOMO/LUMO energy gap were calculated from the spectroscopic and electrochemical data,[51–55] as shown in Table 1.

Table. 1. Optoelectronic data of compounds **1–9**.

Compound	E_g (eV)[a]	λ_{max}em (nm)[b]	λ_{max}abs (nm)	Φ (%)[c]	E_{dox} (V)	HOMO (eV)[d]	LUMO (eV)[e]
1	3.22	436	343	68.25	1.16	–5.41	–2.19
2	3.40	401	314	29.53	1.16	–5.41	–2.10
3	2.97	491	387, 258	48.29	1.17	–5.42	–2.45
4	3.22	430	341, 246	58.26	1.16	–5.41	–2.19
5	3.59	368	305	4.74	1.18	–5.43	–1.84
6	3.40	399	320	29.85	1.11	–5.36	–1.96
7	3.40	479	327	21.24	1.25	–5.50	–2.10
8	3.32	411	333, 254	44.78	1.18	–5.43	–2.11
9	3.54	377	312	6.41	1.14	–5.39	–1.85

[a] Calculated based on the lowest energy absorption edge of the UV absorption spectrum.

[b] Excited at 313 nm in CH_2Cl_2.

[c] Calculated by $\Phi_f = \Phi_{ref}(\Psi_f/\Psi_{ref})(A_{ref}/A_f)(n_f/n_{ref})^2$ where Φ_f is the quantum yield of the unknown, Φ_{ref} is that of the standard, A_{ref} is the absorbance of the standard, A_f is that of the unknown, Ψ_{ref} is the integrated area of the fluorescence intensity of the standard, Ψ_f is that of the unknown, and n_f and n_{ref} are the refractive indices of the solvent used for the unknown and standard, respectively.

[d] F_{c+}/F_{c-} is the inner reference, $E_{HOMO} = -[4.8 + E_{ox}(\text{onset}) - E(F_{c-}/F_{c+})]$ eV, $E(F_{c+}/F_{c-}) = 0.55$ eV, and E_{ox} (onset) is the onset oxidation potential.

[e] LUMO = HOMO + energy gap (eV).

Fig. 2. Emission spectra of **1–9** excited at 313 nm in dichloromethane based on the solutions made as in Fig. 1.

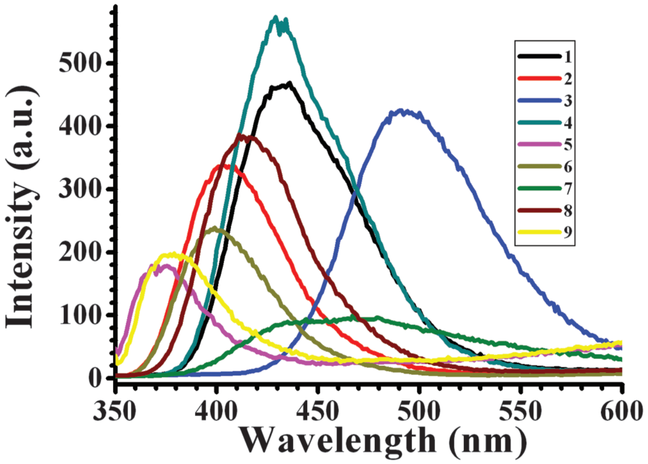
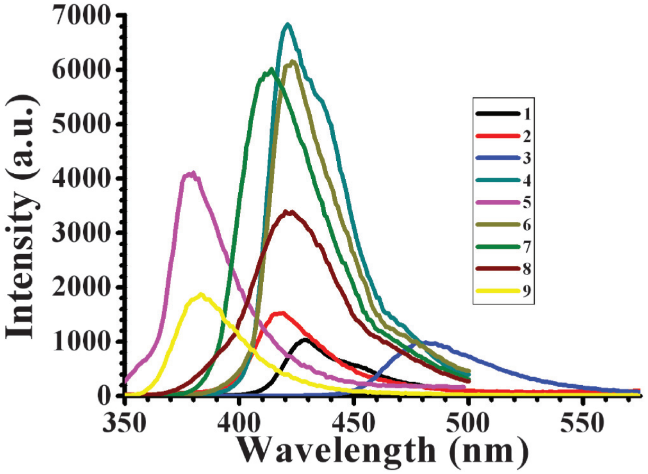


Fig. 3. Emission spectra of **1–9** excited at 313 nm in solid state. The value on the *y*-axis does not mean emission intensity because it changes with slit and filter, etc.



Conclusion

A series of triphenylamine derivatives were synthesized. All compounds exhibit reversible electrochemical behavior. In both CH_2Cl_2 and solid state, the emission of **5** and **9** is violet blue. In CH_2Cl_2, the emission of **2**, **6**, and **8** is deep blue and that of **1**, **4**, and

Fig. 4. 3D-chemdraw of compounds **5**, **1**, and **3**.

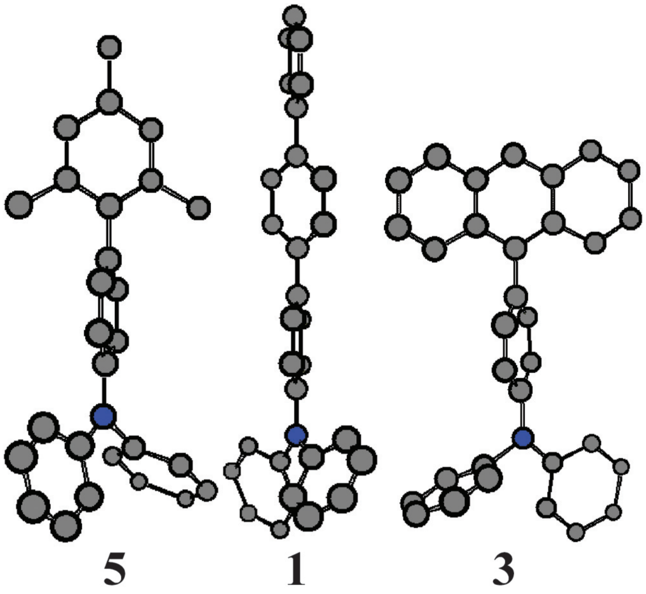


Fig. 5. Emission spectra of compound **3** in different concentrations; it was excited at 313 nm in dichloromethane at room temperature. Inset: the enlarged region.

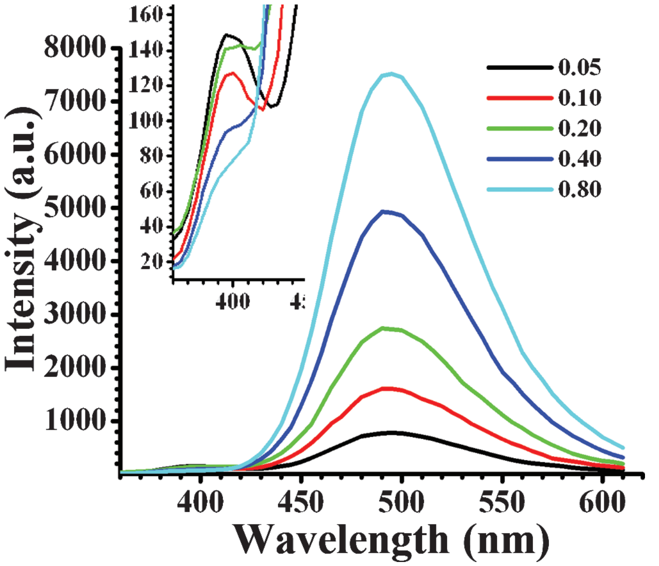
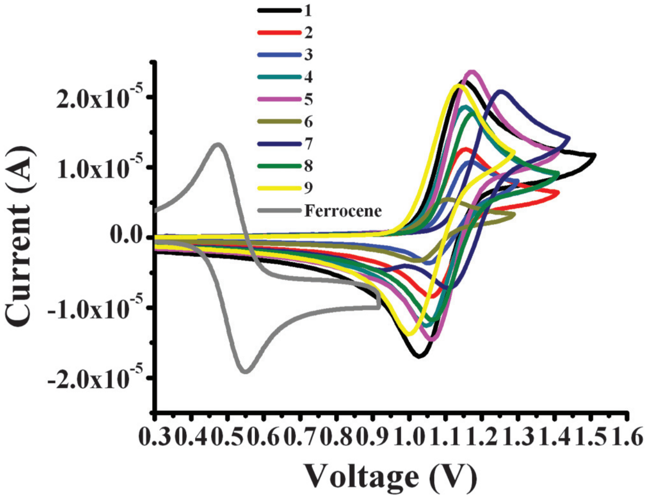


Fig. 6. Cyclic voltammograms of compounds **1–9** measured at a platinum electrode in CH_2Cl_2 – 0.1 mol L^{-1} *n*-Bu_4NClO_4 at a scan rate of 50 mV s^{-1} at 25 °C.



7 is pure blue. Compounds **1**, **4**, and **8** have the best coplanarity as a result, creating the highest quantum yield (44%–68%). Compound **3** emits green, which is assigned as an intermolecular excimer emission. In general, with the properties reported above and the structural similarity with those reported in the literature, these compounds can be potentially useful for blue-emitting, upconverting, and host materials.

Acknowledgement

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