

Synthesis, Photophysical, Electrochemical and Thermal Studies of Triarylamines based on benzo[*g*]quinoxalines

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Abstract. A series of novel dipolar and nonplanar compounds featuring electron acceptor benzo[*g*]quinoxaline and various electron donor triarylamine units have been synthesized in good yields and fully characterized. The photophysical, electrochemical and thermal properties of the synthesized compounds are described. The photoluminescence properties of the synthesized molecules are influenced by peripheral amines. The derivatives have high Stokes shifts, low band gap and the Commission Internationale de l'Eclairage (CIE) coordinates are positioned in the green–yellow region of the chromaticity diagram. The ionization potentials and electron affinity were found to be in the range of 5.11–5.60 eV and 2.77–2.93 eV and are comparable to the commonly used hole transporters. Thermal studies also reveal that these synthesized molecules have good thermal stability with 5% and 10% weight loss temperature ranging from 200 to 355°C and 268 to 442°C, respectively.

Keywords. Benzo[*g*]quinoxaline; triarylamines; green–yellow fluorescent materials; electrochemical; thermal properties.

1. Introduction

In last two decades, after the breakthrough work of Tang and Van Slyke,¹ and Burroughes *et al.*,² extensive investigations have been performed in the development of novel electroluminescent organic materials for organic light emitting devices (OLEDs),^{3–7} Organic field effect transistors (OFETs)⁸ and photovoltaics.^{9,10} Organic π -conjugated molecules with donor–acceptor (D–A) system have attracted great attention due to their unique optical and bipolar charge transport properties useful for OLEDs.^{11,12} The electroluminescence (EL) from such D–A molecules basically originate either from excited states of the D or A moiety and intramolecular charge transfer (ICT) excited states^{13,14} or sometimes even from intermolecular excimers or exciplexes.^{15,16} Thus, appropriate selection of the donor–acceptor units allows us to control photoluminescence properties, HOMO–LUMO energy levels and bandgap of the D–A molecules. Many donor–acceptor molecules have been synthesized for electroluminescence devices which include benzimidazole,^{17,18} quinoxaline,^{19–24} indolo[2,3-*b*]quinoxaline,²⁵ polyquinoxaline,²⁶ pyridoquinoxaline,²⁷ pyrazinoquinoxaline,^{28–30} etc.

Triarylamine derivatives have been extensively utilized as both hole transporter and emissive material in organic electroluminescent devices using molecules

such as anthracene,^{31,32} fluorene,^{33,34} pyrene,^{35,36} carbazole,^{37,38} dibenzothiophene³⁹ since they exhibit low ionization potential, reversible redox potential and bright fluorescence. Further, the triarylamines based on electron–deficient/acceptor units such as benzothiadiazole,⁴⁰ thienopyrazines,⁴¹ quinoxaline⁴² and oxadiazole⁴³ exhibited promising charge (electron and hole) transporting properties which were found to be extremely crucial for the performance of organic electronic devices. In addition to this, their bulky, non-planar structure effectively diminishes the intermolecular π -stacking in the solid state and enhances thermal stability.

In this work, we have synthesized novel bipolar and nonplanar triarylamines based on benzo[*g*]quinoxaline unit and studied their photophysical, electrochemical and thermal properties. The structures of synthesized molecules **2–6** are shown in chart 1.

2. Experimental

2.1 Materials and Methods

All the starting materials and reagents were purchased from commercial sources (Sigma Aldrich and Alfa Aesar) and were used without any further treatment and purification unless otherwise noted. The organic solvents were of HPLC and spectroscopic grade and

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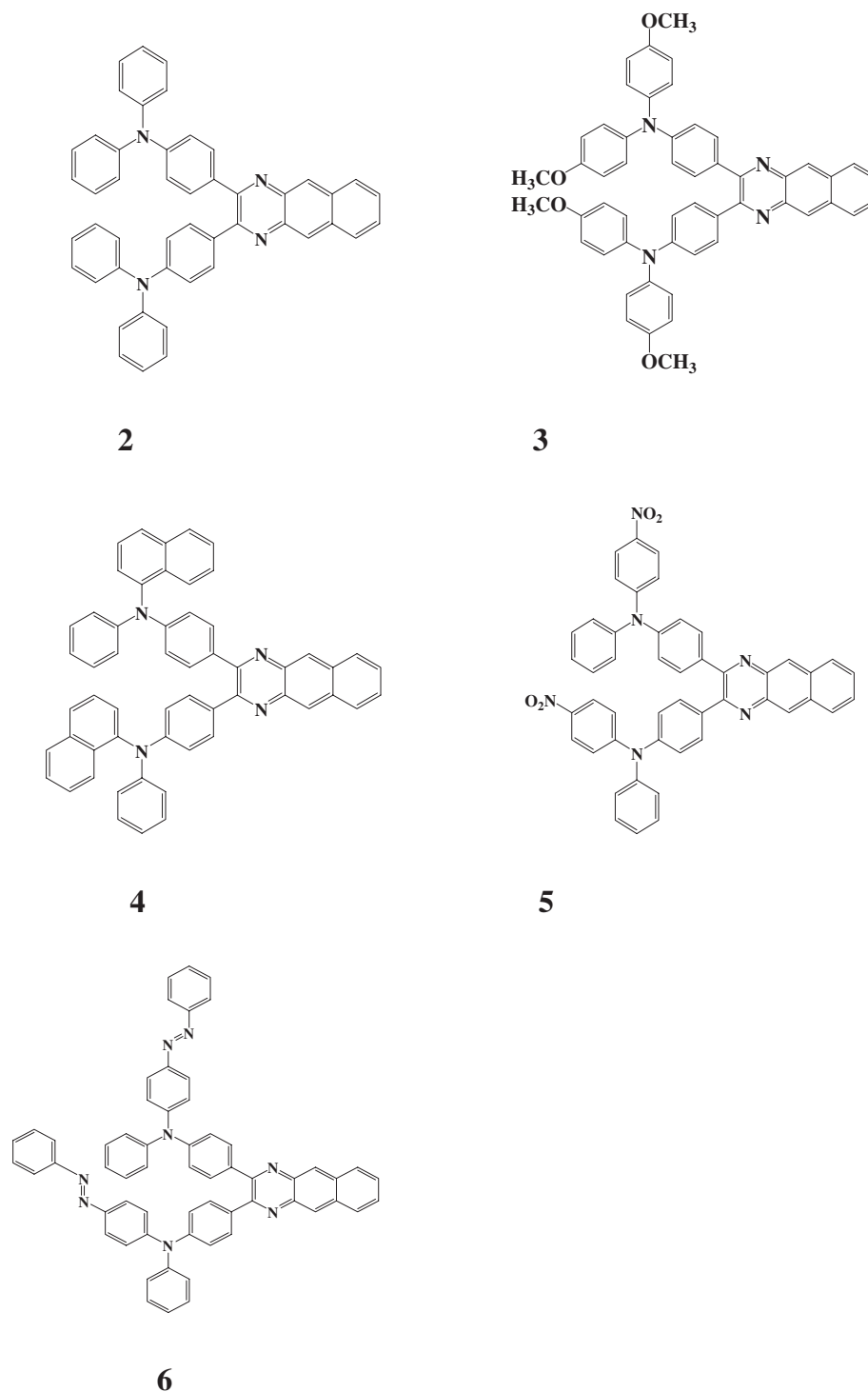


Chart 1. Molecular structures of compounds 2–6.

were dried and freshly distilled using the standard procedures⁴⁴ and handled in moisturefree atmosphere. Column chromatography was carried out using SD–Fine silica gel (60–120 mesh), eluting with n–hexane and chloroform. The progress of reaction and the purity of the compound were checked by thin layer chromatography (TLC) on silica gel coated glass plates, in

which the spots were visualized with UV light (365 nm) and in iodine chamber.

Investigation and confirmation of chemical structures of all the synthesized materials were done using HRMS, FT–IR, ¹H NMR and ¹³C NMR and elemental analysis. ¹H NMR spectra and ¹³C NMR spectra were recorded using CDCl₃ on a Bruker 300 Ultrashield spectrometer

with Tetramethylsilane (TMS) as internal reference at a working frequency of 300 MHz and 75 MHz respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. The spectra of solid compounds were performed in KBr pellets. High resolution Mass spectrometric measurements were recorded on maxis impact 282001.00081 instrument using bruker compass data analysis 4.1 and elemental analysis was carried on EA Euro-elemental analysis instrument.

UV-Visible spectra were recorded in 10^{-5} mol L⁻¹ solutions in toluene, CH₂Cl₂ and CHCl₃ in a 1 cm path length quartz cuvette as well as thermally deposited thin solid films, on SHIMADZU UV-2401PC at room temperature. The excitation and emission spectra were recorded on a Perkin Elmer LS 55 Fluorescence spectrophotometer. Fluorescence quantum yield of the derivatives **2–6** were calculated using tris(8-hydroxyquinolino)aluminium(III) (Alq₃) ($\phi_F = 0.16$ in benzene)⁴⁵ as the standard according to eq. (1).

$$\text{Quantum efficiency } \phi_F = \phi_{\text{ref}} \left(\frac{S_{\text{samp}}}{S_{\text{ref}}} \right) \left(\frac{A_{\text{ref}}}{A_{\text{samp}}} \right) \left(\frac{n_{\text{samp}}^2}{n_{\text{ref}}^2} \right) \quad (1)$$

Where S_{ref} , A_{ref} , n_{ref} and S_{sample} , A_{sample} , n_{sample} represent the integrated emission band area, the absorbance at the excited wavelength, and the refractive index of the solvent, respectively for the standard reference and the sample. The Stokes shifts were also determined and shown in table 2.

Cyclic voltammetry studies was carried out on a computer controlled AUTOLAB PGSTATE 30 electrochemical analyzer equipped with USB electro chemical interface using GPES software version 4.9.005. Typically, a three electrode cell equipped with a glassy

carbon working electrode, Ag/AgCl (non-aqueous) reference electrode and platinum (Pt) wire as counter electrode was employed. The measurements have been carried at room temperature in anhydrous acetonitrile with tetrabutyl ammonium hexafluoro phosphate solution (0.1 M) as supporting electrolyte with a scan rate of 100 mVs⁻¹. The potential of Ag/AgCl reference electrode was calibrated by using ferrocene/ferrocenium redox couple which has the known oxidation potential of + 4.8 eV.⁴⁶

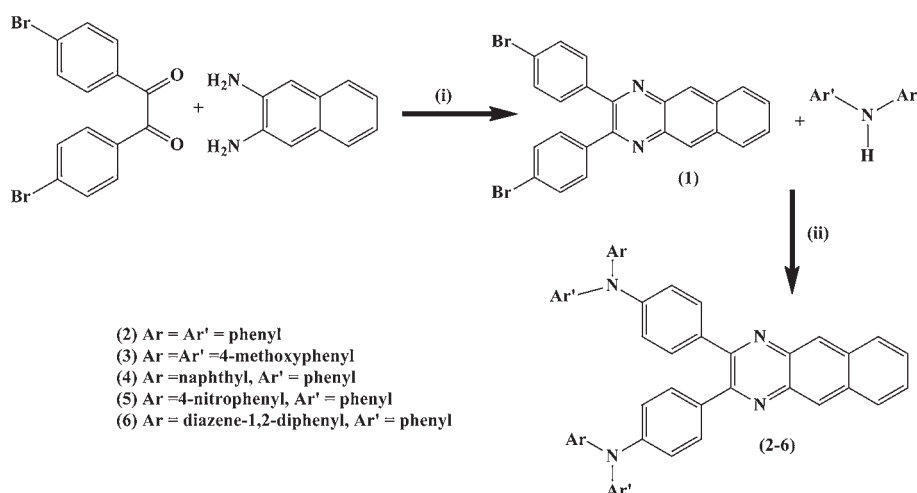
Melting points of the products were less approximately determined by open capillary method. The thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) were performed using Perkin Elmer Pyris Diamond TG/DTA under nitrogen atmosphere.

2.2 Synthesis of the compounds **2–6**

The synthetic protocol used for the preparation of compounds **1–6** is shown in scheme 1. The detailed synthetic procedure and characterization data of compounds **1–6** are given below.

2.2a 2,3-Bis(4-bromophenyl)benzo[*g*]quinoxaline (**1**):

A mixture of 4,4'-dibromobenzil (3.680 g, 10 mmol) and 2,3-diaminonaphthalene (1.582 g, 10 mmol) was dissolved in 20 mL of glacial acetic acid and refluxed for 3 h. The reaction mixture was allowed to cool and then poured over crushed ice to obtain the light green coloured solid. The obtained solid was then dried under vacuum and purified using column chromatography (eluent: n-hexane: chloroform ratio as 70:30) to obtain a bright green solid. Yield: 4.429 g (90.4%), M.p.: 208°C. IR (KBr ν_{max} cm⁻¹): 3056, 2922,



Scheme 1. Synthesis of compounds **2–6**. Reaction conditions: (i) gl. CH₃COOH, Reflux, 3 h; (ii) Pd₂(dba)₃, SPhos, t-BuONa, Reflux, N₂ atmosphere, 4–10 h.

2852, 1585 (–C=N str), 1068; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.70 (s, 2H, ArH), 8.10 (dd, 2H, ArH, $J = 3.3, 3.0$ Hz), 7.41–7.58 (m, 10H, ArH); ^{13}C NMR: 152.46, 137.77, 137.72, 134.23, 131.61, 131.38, 128.53, 127.60, 126.96, 123.89. Anal. Calcd for $\text{C}_{24}\text{H}_{14}\text{Br}_2\text{N}_2$: C (58.81), H (2.88), N (5.71), Br (32.60). Found: C (58.79), H (2.86), N (5.74), Br (32.61).

2.2b 2,3-Bis[4-(*N*-phenylbenzeamino)phenyl]benzo[*g*]quinoxaline (2): A mixture of compound **1** (490 mg, 1 mmol) and diphenylamine (338 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution $\text{Pd}_2(\text{dba})_3$ (37 mg, 0.04 mmol), SPhos (25 mg, 0.06 mmol) and *t*-BuONa (300 mg, 3.1 mol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 4 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane) to obtain a bright yellow solid. Yield: 614 mg (92.0%), M.p.: 249°C. IR (KBr_{vmax} cm^{-1}): 3037, 2922, 2852, 1585 (–C=N str), 1485, 1270 (–C–N str); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.78 (s, 2H, ArH), 8.15 (dd, 2H, ArH, $J = 3.3$ Hz), 7.50–7.57 (m, 6H, ArH), 7.25–7.31 (m, 8H, ArH), 7.03–7.25 (m, 16H, ArH); ^{13}C NMR: 153.76, 148.90, 147.18, 137.58, 133.93, 132.02, 130.92, 129.39, 128.50, 126.98, 126.61, 125.12, 123.63, 121.78; HRMS calcd for $\text{C}_{48}\text{H}_{35}\text{N}_4$ 667.2856, found 667.2851. Anal. Calcd for $\text{C}_{48}\text{H}_{34}\text{N}_4$: C (86.46), H (5.14), N (8.40). Found: C (86.44), H (5.13), N (8.44).

2.2c 2,3-Bis[4-(4-methoxy-*N*-(4-)benzeamino)phenyl]benzo[*g*]quinoxaline (3): A mixture of compound **1** (490 mg, 1 mmol) and 4,4'-dimethoxydiphenyl amine (462 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution $\text{Pd}_2(\text{dba})_3$ (37 mg, 0.04 mmol), SPhos (25 mg, 0.06 mmol) and *t*-BuONa (300 mg, 3.1 mol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 6 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane: chloroform ratio as 70:30) to obtain a bright red solid. Yield: 760 mg (96.0%), M.p.: 263°C. IR (KBr_{vmax} cm^{-1}): 3040, 2923, 2834, 1591 (–C=N str), 1235 (–C–N str); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.65 (s, 2H, ArH), 8.03 (dd, 2H, ArH, $J = 3.3, 3.0$ Hz), 7.44–7.52 (m, 6H, ArH), 7.07–7.12 (m, 8H, ArH), 6.83–6.90 (m, 12H, ArH), 3.80 (s, 12H, –OCH₃); ^{13}C NMR: 156.30, 154.02, 149.60, 140.30, 137.80, 133.77, 130.74, 130.55, 128.44, 127.11,

126.85, 126.35, 118.92, 114.77, 55.48; HRMS calcd for $\text{C}_{52}\text{H}_{43}\text{N}_4\text{O}_4$ 787.3201, found 787.3206. Anal. Calcd for $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_4$: C (79.37), H (5.38), N (7.12), O (8.13). Found: C (79.35), H (5.36), N (7.15), O (8.14).

2.2d 2,3-Bis[4-(*N*-phenyl-2-naphthylamino)phenyl]benzo[*g*]quinoxaline (4): A mixture of compound **1** (490 mg, 1 mmol) and *N*-naphthylphenylamine (438 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution $\text{Pd}_2(\text{dba})_3$ (37 mg, 0.04 mmol), SPhos (25 mg, 0.06 mmol) and *t*-BuONa (300 mg, 3.1 mol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 5 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography eluent: *n*-hexane: chloroform ratio as 80:20 to obtain a bright yellow solid. Yield: 722 mg (94.0%), M.p.: 342°C. IR (KBr_{vmax} cm^{-1}): 3044, 2922, 1587 (–C=N str), 1267 (–C–N str); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.64 (s, 2H, ArH), 8.02 (dd, 2H, ArH, $J = 3.3, 3.0$ Hz), 7.76–7.86 (m, 6H, ArH), 6.87–7.50 (m, 26H, ArH); ^{13}C NMR: 153.94, 149.31, 147.63, 143.00, 137.85, 135.30, 133.82, 131.50, 131.06, 130.84, 129.23, 128.44, 128.40, 127.29, 127.01, 126.81, 126.43, 126.29, 126.21, 124.13, 123.16, 122.78, 119.88; HRMS calcd for $\text{C}_{56}\text{H}_{39}\text{N}_4$ 767.3169, found 767.3172. Anal. Calcd for $\text{C}_{56}\text{H}_{38}\text{N}_4$: C (87.70), H (4.99), N (7.31). Found: C (87.72), H (4.96), N (7.32).

2.2e 2,3-Bis[4-(4-nitro-*N*-phenylbenzeamino)phenyl]benzo[*g*]quinoxaline (5): A mixture of compound **1** (490 mg, 1 mmol) and 4-nitrodiphenylamine (472 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution $\text{Pd}_2(\text{dba})_3$ (37 mg, 0.04 mmol), SPhos (25 mg, 0.06 mmol) and *t*-BuONa (300 mg, 3.1 mol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 10 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane: chloroform ratio as 60:40) to obtain a bright yellow solid. Yield: 210 mg (53.17%), M.p.: 314°C. IR (KBr_{vmax} cm^{-1}): 3051, 2921, 1580 (–C=N), 1489, 1286 (–C–N str), 1108; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.89 (s, 2H, ArH), 8.18 (dd, 2H, ArH, $J = 3.3, 3.0$ Hz), 8.08 (d, 4H, ArH, $J = 9.3$ Hz), 7.62 (d, 6H, ArH, $J = 6.6$ Hz), 7.03–7.42 (m, 18H, ArH); ^{13}C NMR: 152.72, 147.52, 145.33, 141.30, 134.54, 131.72, 130.21, 128.69, 127.62, 126.83, 126.36, 125.47, 124.59, 120.05; HRMS calcd for $\text{C}_{48}\text{H}_{33}\text{N}_6\text{O}_4$ 757.2558, found 757.2577. Anal. Calcd for

C₄₈H₃₂N₆O₄: C (76.17), H (4.25), N (8.46), O (11.10). Found: C (76.17), H (4.23), N (8.49), O (11.12).

2.2f 2,3-Bis[4-(*N*-phenyl-4-(2-phenyldiazenyl)benzaminophenyl)]benzo[g]quinoxaline (**6**): A mixture of compound **1** (490 mg, 1 mmol) and 4-(phenylazo)diphenylamine (592 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution Pd₂(dba)₃ (37 mg, 0.04 mmol), SPhos (25 mg, 0.06 mmol) and *t*-BuONa (300 mg, 3.1 mol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 7 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane: chloroform ratio as 65:35) to obtain red solid. Yield: 401 mg (56.0%), M.p.: 225°C. IR (KBr_ν_{max} cm⁻¹): 3036, 2922, 2855, 1585 (–C=N str) 1489, 1269 (–C–N str); ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.77 (s, 2H, ArH), 8.10 (dd, 2H, ArH, *J* = 3.3, 3.0 Hz), 7.84–7.89 (m, 8H, ArH), 7.15–7.59(m, 30H, ArH); ¹³C NMR: 153.37, 152.80, 149.84, 148.20, 147.91, 146.46, 137.40, 134.11, 133.16, 131.20, 130.42, 129.74, 129.03, 128.56, 127.09, 126.05, 124.84, 124.35, 123.36, 123.09, 122.61; HRMS calcd for C₆₀H₄₃N₈ 875.3605, found 875.3596. Anal. Calcd for C₆₀H₄₂N₈: C (82.36), H (4.84), N (12.81). Found: C (82.33), H (4.89), N (12.78).

3. Results and Discussion

3.1 Synthesis and characterization

2,3-Bis(4-bromophenyl)benzo[g]quinoxaline (**1**) was prepared by condensing 4,4'-dibromobenzil and 2,3-diaminonaphthalene in glacial acetic acid. Compounds **2–6** were synthesized by using palladium catalyzed Buchwald–Hartwig amination reaction^{47,48} by treating compound **1** with the corresponding diarylamine in the presence of tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃), 2-dicyclohexylphosphino-2', 6'-dimethoxybiphenyl (SPhos) and sodium tertiarybutoxide(*t*-BuONa) in toluene. For the synthesis of compounds **2–6** we have also tried other catalyst combinations such as Pd(OAc)₂/XantPhos, Pd(dba)₂/XantPhos, Pd(dba)₂/DPPF and found that they worked equally well. However, the use of Pd₂(dba)₃/SPhos catalyst combination significantly reduces the reaction time with good yield as compared to the above three combinations. The synthesized compounds **2–6** are yellow to red solid soluble in common organic solvents including dichloromethane, toluene, chloroform, acetonitrile, etc. However, they are sparingly soluble in

methanol and insoluble in water. All the target compounds were confirmed by FT-IR, ¹H, ¹³C NMR, high resolution mass spectroscopy and elemental analysis.

3.2 Photophysical properties

The absorption and fluorescence properties of compounds **2–6** were studied in solvents of varying polarity (toluene, dichloromethane and chloroform) and solid thin film. The synthesized molecules show similar UV-Vis absorption spectra in all three solvents and thin solid film (figure 1a). The absorption spectra of all the synthesized molecules in the above mentioned solvents and thin solid film reveal two major bands arising due to π–π* (300–315 nm) transition within the arylamine units and the benzo[g]quinoxaline core and lower energy charge transfer transition (407–495 nm) from various electron donor triarylamine to electron acceptor benzo [g]quinoxaline segment. In addition, an n–π* transition originating from the terminal arylamine moiety is expected to appear below 300 nm, but it is probably overlapping with the intense π–π* transitions.

Further, in the absorption spectra of compounds **5** and **6** (figure 1a) in above mentioned solvents and solid thin film, the intensity of charge transfer transition (407–450 nm) is high as compared to other derivatives suggesting better charge transfer due to electron withdrawing group like –NO₂ and diazene group on triarylamine moiety.

The emission peaks of compounds **2–6** in the toluene are in the range of 510–555 nm (figure 1b) with a bathochromic shift as the thin film ranging from 532–596 nm (see supplementary information). A significant bathochromic shift of 41 nm is observed in solid thin film of compound **2** as compared to toluene due to electron donating methoxy group on triarylamine moiety. The emission intensity of compound **6** in toluene is too low which may, due to presence of diazene group on triarylamine moiety and thus showing influence of peripheral amine on emission intensity. On increasing polarity of solvent from toluene to CH₂Cl₂ and CHCl₃, compounds **2** and **4** emit with red shift of around 44–61 nm. However compound **3**, **5** and **6** do not emit in CH₂Cl₂ and CHCl₃ suggesting nonradiative relaxation from excited state to ground state in polar solvents.

The colour quality of the emitted light is adjudged by means of Commission International de l'Éclairage (CIE) coordinates. The CIE chromaticity coordinates were determined by using emission spectra of compounds **2–6** excited at 550 nm in solid thin film. The

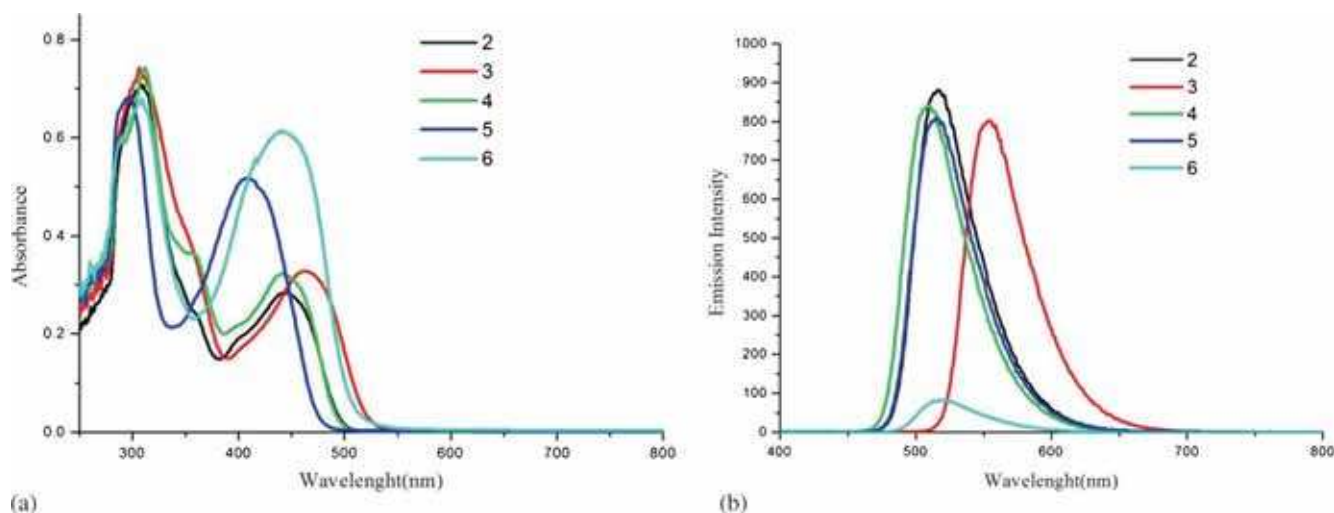


Figure 1. UV-Vis absorption spectra (a) and emission spectra; (b) of compounds 2–6 in toluene. (see supplementary information for spectra in CH_2Cl_2 , CHCl_3 and solid thin film).

obtained CIE coordinates are located in green–yellow region (see supplementary information).

Other basic photophysical characteristics such as the molar extinction coefficient ($\log \epsilon$), optical band gaps (E_g^{opt}), Stokes shift ($\nu_{\text{Abs}} - \nu_{\text{Em}}$) and fluorescent quantum yield (ϕ_F) of the molecules were determined and summarized in tables 1 and 2.

3.3 Electrochemical properties

Electrochemical property of the synthesized derivatives was measured by cyclic voltammetry in dichloromethane solution using ferrocene as an internal standard to calibrate the redox potentials. On anodic sweep, two quasi-reversible waves were observed for all the synthesized compounds 2–6 (figures 2a and 2b) which may be due to the oxidation of triarylamine moiety corresponding to two electrons.⁴⁹ E_{ox} potential decreases on increasing donor strength (3 > 4 > 2).

On cathodic sweep, one reversible wave was observed for all the compounds (see supplementary information) corresponding to the reduction of benzo[g]quinoxaline

segment.⁵⁰ On cathodic sweep an irreversible wave was observed for compound 5 at -1.30 V which may be due to the reduction of $-\text{NO}_2$ group.

The HOMO and LUMO energy levels of the synthesized materials 2–6 are in the range of 5.11–5.60 eV and 2.77–2.93 eV, respectively which are comparable to the commonly used triarylamine based hole transporting materials such as N,N' -(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) (HOMO = -5.50 eV and LUMO = -2.3 eV) and N,N' -Di(1-naphthyl)- N,N' -diphenyl(1,1'-biphenyl)-4,4'-diamine (α -NPD) (HOMO = -5.50 eV and LUMO = -2.4 eV). Thus, the synthesized molecules might act as hole transporting materials. The energy band gap calculated from the cyclic voltammetry measurements are in range of 2.25–2.82 eV which are in close agreement with optical band gap. The observed parameters are reported in table 3.

3.4 Thermal properties

The thermal stability of the synthesized molecules 2–6 (table 3) was determined by Thermogravimetric

Table 1. Absorption and Emission data of compounds 2–6.

Compd.	λ_{abs} (nm) ^a				λ_{em} (nm) ^b				$\log \epsilon^b$
	toluene	CH_2Cl_2	CHCl_3	film	toluene	CH_2Cl_2	CHCl_3	film	
2	308,443	304,445	310,452	308, 449	517	578	568	532	4.853
3	306,463	306,464	300,470	293,358,495	555			596	4.863
4	312,441	310,446	312,449	315,446	510	569	554	551	4.873
5	297,407	297,415	300,416	298,429	516			539	4.835
6	309,439	306,439	308,445	305,450	520			540	4.831

^aRecorded in 10^{-5} mol L⁻¹ solution in toluene, CH_2Cl_2 , CHCl_3 and in thin solid film form.

^b ϵ is Extinction coefficient (L mol⁻¹ cm⁻¹) measured in toluene.

Table 2. Optical bandgap, Stoke shift, Quantum yield and CIE Coordinates for compounds 2–6.

Compd	E_g^{opt} (eV) ^a	Stokes shift (cm ⁻¹) ^b		ϕ_F ^c	CIE coordinates ^d	
	film	toluene	film		x	y
2	2.39	13125	13492	0.40	0.364	0.409
3	2.30	14661	16778	0.59	0.427	0.378
4	2.42	12443	13597	0.45	0.432	0.465
5	2.43	14290	15004	0.38	0.398	0.463
6	2.45	13131	13918	0.04	0.393	0.405

^aOptical bandgap estimated from the optical edge of spectrum in thin solid film.

$$E_g^{opt} = \left(\frac{1240.8}{\lambda_{opt\ edge}} \right) \text{eV}$$

^bStokes shift calculated from absorption and emission wavelengths observed in solution and thin solid film.

^cQuantum yield with reference to Alq₃ ($\phi_F = 0.16$ in benzene).⁴⁵

^dMeasured in solid thin film.

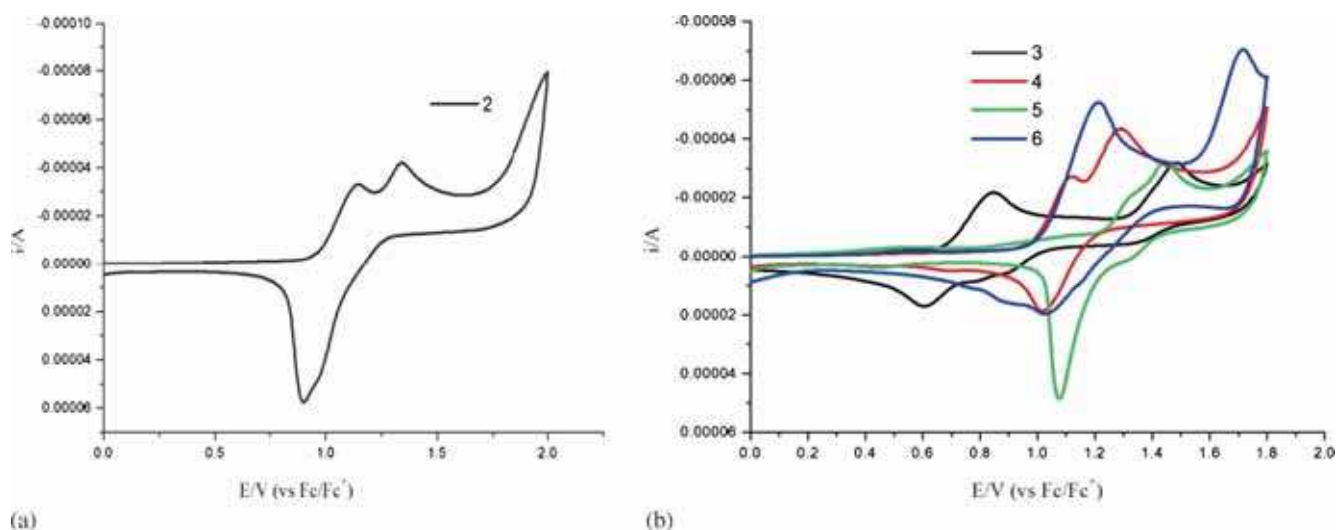


Figure 2. The cyclic voltammogram (anodic sweep) of (a) compound 2, and; (b) compounds 3–6, measured in anhydrous CH₂Cl₂ solution against ferrocene/ferrocenium at 100 mV/sec.

Table 3. Electrochemical and thermal data of compounds 2–6.

Compd	$E_{ox}^{peak\ a}$	$E_{red}^{peak\ b}$	HOMO ^c	LUMO ^d	$E_g^{EC\ e}$	T_d (°C) ^f	T_m (°C) ^g	T_{max} (°C) ^h
2	1.139, 1.338	-1.497	-5.38	-2.93	2.44	277(385)	249	571
3	0.848, 1.492	-1.556	-5.11	-2.85	2.25	355(442)	263	575
4	1.116, 1.294	-1.520	-5.39	-2.89	2.50	292(423)	342	593
5	1.331, 1.439	-1.547	-5.60	-2.77	2.82	207(268)	314	582
6	1.211, 1.715	-1.627	-5.44	-2.81	2.62	200(348)	225	584

^a E_{ox}^{peak} oxidation peak potential (V).

^b E_{red}^{peak} reduction peak potential (V).

^cHOMO energy level calculated from $E_{HOMO} = -[E_{ox}^{peak} - E_{redox}(Fc/Fc^+) + 4.8]$ eV.

^dLUMO energy calculated from $E_{LUMO} = -[E_{red}^{peak} - E_{redox}(Fc/Fc^+) + 4.8]$ eV.

^e E_g^{EC} calculated from $E_g^{EC} = [HOMO - LUMO]$ eV.

^fDecomposition temperature at 5% and 10% (in parentheses) weight loss in TGA.

^gMelting point determined by open capillary method

^hDerivative weight loss.

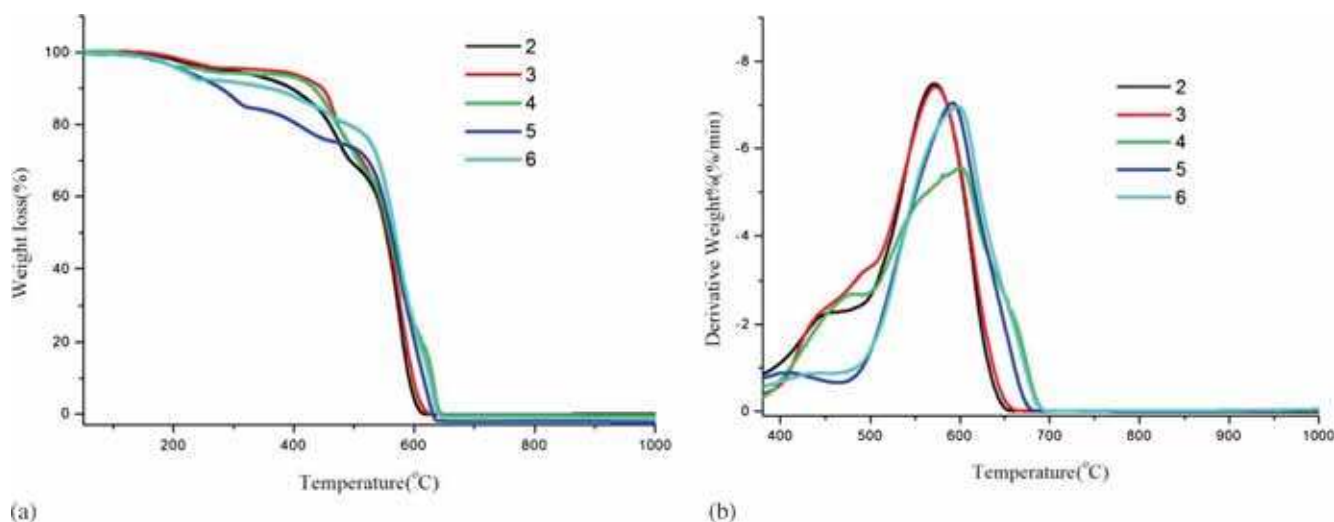


Figure 3. (a) TGA thermogram and (b) Derivative weight loss of compounds **2–6** under nitrogen atmosphere at normal pressure. Heating rate, 10°C/min.

analysis (TGA) and Differential Thermal Analysis (DTA).

TGA thermogram (figure 3a) of compounds **2–6** reveals that these derivatives have high thermal stability with no weight loss at low temperature and are comparable to the commonly used hole-transporting materials such as 9,10-bis(diphenylamino)anthracene (PPA), 9,10-bis(1-naphthylphenylamino)anthracene (NPA), TPD, 4,4'-bis(1-naphthylphenylamino)biphenyl (NPB) with stability in range 185–382°C.^{51,52} The decomposition temperature corresponding to 5% and 10% weight losses were in the range of 200–355°C and 268–442°C, respectively. The order of thermal stability among the synthesized derivatives is **3**>**4**>**2**>**5**>**6**. Melting points of the derivatives **2–6** are in the range of 225–342°C. The derivative TGA plot (figure 3b) shows narrow derivative peak, indicating high decomposition temperature with T_{\max} in the range of 571–593°C. The sharp endothermic peak is observed for all compounds in the DTA plot (see supplementary information) at their respective melting points and exothermic peak is observed above 500°C for all the synthesized molecules suggesting that no crystallization is taking place upto 500°C.

4. Conclusions

Triarylamine based on benzo[*g*]quinoxaline compounds have been synthesized via palladium-catalyzed C–N bond formation reaction using Pd₂(dba)₃/SPhos catalyst system in good yields. The absorption, emission, electrochemical and thermal properties of the synthesized materials are significantly influenced by the nature of the peripheral amine segments attached to the

benzo[*g*]quinoxaline core. The emission colour of these materials was tuned from green to yellow by changing the nature of the diarylamines. The electrochemical investigation of the synthesized molecules shows that the ionization potentials and electron affinities are comparable to the most commonly used hole-transporting materials. Thermal properties revealed that the derivatives have high melting point and good thermal stability. The results indicate that the synthesized molecules are promising candidates for hole transporting application in organic electronics.

Supplementary Information

All additional information pertaining to compounds **2–6**, namely, absorption and emission spectra in CH₂Cl₂, CHCl₃ and solid thin films (figures S1 and S2), Chromaticity diagrams (figures S3), Cyclic voltammograms (cathodic sweep) (figures S4 and S5), DTA plot (figure S6), HRMS spectra (figure S7), FTIR spectra (figure S8), ¹H and ¹³C NMR spectra (figures S9 and S10), Photographs (figures S11 and S12) are given in the supporting information. Supplementary Information is available at www.ias.ac.in/chemsci.

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