Hexaphenylphenylene dendronised pyrenylamines for efficient organic light-emitting diodes

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A series of blue-emitting triarylamines containing pyrene and hexaphenylbenzene dendrons were successfully synthesized by employing the Diels–Alder and palladium catalyzed C–N coupling reactions. They display high glass transition temperatures (>140 °C) in differential scanning calorimetry and facile reversible oxidation couple in cyclic voltammetry. They are also thermally stable exhibiting decomposition temperature above 385 °C. Efficient blue-emitting electroluminescent devices were fabricated using these novel amines as the hole transporting layer and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) as the electron transporting layer. Colour mixing or green emission was observed when tris(8-hydroxyquinoline)aluminium (Alq_3) was used as the electron transporting layer. However insertion of a thin layer of TPBI or 1,3,5-tris(4-*tert*-butylphenyl-1,3,4-oxadiazolyl)benzene (TPOB) in between the HTL and Alq_3 layers led to pure blue emission owing to the confinement of recombination inside the HTL layer containing the compounds.

Introduction

It is necessary to develop organic or organometallic compounds with appropriate colour (blue, green and red) chromaticity for efficient translation of organic light-emitting diode (OLED) technology into practical flat-panel display applications.[1,2] Though organic small molecules and polymers have been intensively sought for applications in OLED for a decade now, recent phosphorescent devices fabricated using triplet emitters such as cyclometallated iridium(III) complexes decreased the dominance of organic compounds in the OLED field. Though the organometallic triplet emitters are performing efficiently their cost is high and only green and red emitters have been realized so far with exceptional performance.[3] Blue-emitting organometallic complexes are scarce and their device fabrication is also limited by the non-availability of suitable triplet hosts.[4] Hence blue-emitting organic compounds that display colour purity and good performance statistics in electroluminescent devices (EL) are attractive.[5] Organic materials reported to emit blue colour in EL are mostly polymeric in nature.[6] Organic small molecules derived from fluorene[7] or bifluorene[8] motifs have been found to perform efficiently in OLED with bright blue emission. Triarylamines containing polyaromatics such as pyrene,[9] carbazole[10] and anthracene[11] have been demonstrated as efficient emitting hole transporters. Only anthracene based amines exhibited promising blue EL performance while others displayed red-shifted emission with green or yellow colours. Recently Müllen *et al.* demonstrated that large molecular architectures can be assembled utilizing hexaphenylbenzene building blocks that are readily available from the Diels–Alder reaction of alkynes and cyclopentadienone.[12] These polyphenyl dendrimers possessed unique photophysical properties and thermal stability. Small molecules based on polyphenylbenzene motifs have been utilized to arrive at electroluminescent materials emitting blue[13] and red[14] colours. In this article we broaden the application of the hexaphenylbenzene core in the construction of organic materials suitable for OLED fabrication by tethering it with pyrenylamine which is a strong blue emitter. We observe a narrow blue emission for these conjugates and they additionally display marked thermal robustness. These two properties make them suitable for electroluminescent applications.

Experimental

General information

Unless otherwise specified, all reactions and manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh). Dichloromethane and toluene were distilled from calcium hydride and Na/benzophenone respectively under nitrogen atmosphere.

Instrumentation

All the reactions were performed under inert atmosphere unless otherwise specified. ^1H spectra were recorded on a Bruker AC300 spectrometer operating at 300.135 MHz. Mass spectra (FAB) were recorded on a Hewlett-Packard GC/MS 5995 spectrometer. Elemental analyzes were performed on a Perkin-Elmer 2400 CHN analyzer. Electronic absorption spectra were measured on a Cary 50 Probe UV-visible spectrometer. Emission spectra were recorded by a Hitachi fluorescence spectrometer (F4500). Emission quantum yields

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were obtained by the method of Demas and Crosby[15] using Coumarin-I (Φ_F = 0.99 in ethyl acetate) as reference. Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum auxiliary electrode and a non-aqueous Ag/AgNO$_3$ reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p{}^a + E_p{}^c)$, where $E_p{}^a$and $E_p{}^c$ are the anodic and cathodic peak potentials, respectively. All potentials reported are referenced to ferrocene which was used as internal standard toward the end of each experiment. The solvent in all experiments was CH$_2$Cl$_2$ and the supporting electrolyte was 0.1 M^{-1} tetrabutylammonium hexafluorophosphate. DSC measurements were carried out on a Perkin-Elmer differential scanning calorimeter at a heating rate of 10 °C min^{-1} and a cooling rate of 30 °C min^{-1} under nitrogen atmosphere. TGA measurements were performed on a TA-7 series thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under a flow of nitrogen. The OLED fabrication procedure is elaborted in detail in an earlier report.[10a]

Synthesis

The precursors 1,3-bis(4-bromophenyl)propan-2-one,[16] 1,2-bis-(4-*tert*-butylphenyl)ethyne,[17] 1-bromo-4-((4-methoxyphenyl)-ethynyl)benzene[18] and 1,2-bis(4-methoxyphenyl)ethyne[19] were prepared by following the literature procedures. The synthesis of **B7** was described earlier.[14]

3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (3). A mixture of 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (2.70 g, 10 mmol), 1,3-diphenylpropan-2-one (2.10 g, 10 mmol) and ethanol (50 mL) was heated to 80 °C and KOH (0.56 g, 10 mmol) added at once. An exothermic reaction was followed by a dark purple solid precipitation. The solids were collected by filtration, washed thoroughly with ethanol (3 × 30 mL) and dried. Yield: 3.84 g (86%). Dark purple solid. MS (FAB): *m*/*z*: 444.2 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 3.77 (s, 6 H), 6.68–6.71 (m, 4 H), 6.82–6.85 (m, 4 H), 7.21–7.23 (m, 10 H).

3,4-Bis(4-*tert*-butylphenyl)-2,5-diphenylcyclopenta-2,4-dienone (4). Prepared from 1,2-bis(4-*tert*-butylphenyl)ethane-1,2-dione as described above in 89% yield. Dark purple solid. MS (FAB): *m*/*z*: 496.3 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 1.22 (s, 18 H), 6.79–6.82 (m, 4 H), 7.11–7.15 (m, 4 H), 7.18–7.23 (m, 10 H).

5. A mixture of 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (4.45 g, 10 mmol), 1-bromo-4-(2-(4-methoxyphenyl)ethynyl)benzene (3.16 g, 11 mmol) and diphenyl ether (10 mL) were heated to 200 °C for 3 h during which the dark purple colour vanished. It was cooled and poured into cold methanol. The colourless precipitate formed was filtered, washed with methanol and dried. Further purification was performed by column chromatography on silica gel and hexane–dichloromethane mixture (1 : 1) as eluent. Yield: 6.54 g (93%). Colourless solid. MS (FAB): *m*/*z*: 704.2 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 3.59 (s, 6 H), 3.61 (s, 3 H), 6.37–6.41 (m, 6 H), 6.63–6.68 (m, 8 H), 6.74–6.78 (m, 4 H), 6.82–6.87 (m, 6 H), 6.95–6.98 (m, 2 H).

6. Obtained in 77% from 3,4-bis(4-*tert*-butylphenyl)-2,5-diphenylcyclopenta-2,4-dienone and 1-(2-(4-*tert*-butylphenyl)-ethynyl)-4-bromobenzene as described above. Colourless solid. MS (FAB): *m*/*z*: 782.3 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 1.07 (s, 18 H), 1.11 (s, 9 H), 6.60–6.66 (m, 8 H), 6.77–6.85 (m, 16 H), 6.91–6.95 (m, 2 H).

7. Synthesized in 88% yield from 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone and 1-(2-(4-*tert*-butylphenyl)ethynyl)-4-bromobenzene as described above for **5**. Colourless solid. MS (FAB): *m*/*z*: 756.3 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 1.11 (s, 9 H), 3.60 (s, 6 H), 6.37–6.40 (m, 4 H), 6.62–6.68 (m, 8 H), 6.76–6.87 (m, 12 H), 6.91–6.94 (m, 2 H).

2,5-Bis(4-bromophenyl)-3,4-bis(4-methoxyphenyl)cyclopenta-2,4-dienone (8). Yield: 72%. Purple solid. MS (FAB): *m*/*z*: 602.0 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 3.78 (s, 6 H), 6.69–6.73 (m, 4 H), 6.79–6.82 (m, 4 H), 7.06–7.10 (m, 4 H), 7.33–7.37 (m, 4 H).

2,5-Bis(4-bromophenyl)-3,4-bis(4-*tert*-butylphenyl) cyclopenta-2,4-dienone (9). Yield: 84%. Purple solid. MS (FAB): *m*/*z*: 654.1 (M$^+$). ^{1}H NMR (CDCl$_3$, δ): 1.25 (s, 18 H), 6.74–6.78 (m, 4 H), 7.07–7.11 (m, 4 H), 7.12–7.16 (m, 4 H), 7.32–7.36 (m, 4 H).

10. Yield: 89%. Colourless solid. MS (FAB): *m*/*z*: 812.6 (M$^+$). Anal. Calcd. for C$_{46}$H$_{36}$Br$_2$O$_4$: C, 67.99; H, 4.47. Found: C, 67.78; H, 4.36%. ^{1}H NMR (CDCl$_3$, δ): 3.62 (s, 12 H), 6.38–6.43 (m, 8 H), 6.60–6.64 (m, 12 H), 6.96–6.99 (m, 4 H).

11. Yield: 80%. Colourless solid. MS (FAB): *m*/*z*: 916.9. Anal. Calcd. for C$_{58}$H$_{60}$Br$_2$: C, 75.98; H, 6.60. Found: C, 76.01; H, 6.54%. ^{1}H NMR (CDCl$_3$, δ): 1.10 (s, 36 H), 6.59–6.62 (m, 8 H), 6.65–6.69 (m, 4 H), 6.79–6.83 (m, 8 H), 6.92–6.96 (m, 4 H).

12. Yield: 76%. Colourless solid. MS (FAB): *m*/*z*: 864.7 (M$^+$). Anal. Calcd.for C$_{52}$H$_{48}$Br$_2$O$_2$: C, 72.22; H. 5.59. Found: C, 72.05; H, 5.37%. ^{1}H NMR (CDCl$_3$, δ): 1.10 (m, 18 H), 3.63 (s, 6 H), 6.39–6.44 (m, 4 H), 6.57–6.60 (m, 4 H), 6.63–6.67 (m, 8 H), 6.79–6.82 (m, 4 H), 6.94–6.97 (m, 4 H).

B1. A mixture of **5** (1.40 g, 2 mmol), *N*-phenylpyren-1-amine (0.65 g, 2.2 mmol), potassium *tert*-butoxide (0.288 g, 3 mmol), Pd(dba)$_2$ (11.4 mg, 0.02 mmol), tri-*tert*-butylphosphine (6 mg, 0.03 mmol) and toluene (20 mL) was heated at 80 °C for 8 h. After it cooled, water and diethyl ether were added and the organic layer was separated. It was dried over anhydrous MgSO$_4$ and evaporated to dryness to leave the crude product. It was purified further by column chromatography on silica gel using a hexane–dichloromethane mixture (2 : 3). Yield: 1.62 g (88%). Yellow solid. MS (FAB): *m*/*z*: 995.5 (M + H). Anal. Calcd. for C$_{76}$H$_{67}$N: C, 91.80; H, 6.79; N, 1.41. Found: C, 91.72; H, 6.81; N, 1.34%. ^{1}H NMR (CDCl$_3$, δ):1.09 (s, 18 H), 1.24 (s, 9 H), 6.57–6.68 (m, 8 H), 6.73–6.93 (m, 20 H), 7.09

(t, J = 7.8 Hz, 2 H), 7.58 (d, J = 8.2 Hz, 1 H), 7.84 (d, J = 8.2 Hz, 1 H), 7.92–81.5 (m, 8 H).

B2. Prepared from *N*-phenylpyren-1-amine and **6** as described above. Yield: 75%. Yellow solid. MS (FAB): *m*/*z*: 917.1 (M + H). Anal. Calcd. for $C_{67}H_{49}NO_3$: C, 87.84; H, 5.39; N, 1.53. Found: 87.55; H, 5.26; N, 1.48%. Found: ^{1}H NMR ($CDCl_3$, δ): 3.59 (s, 3 H), 3.61 (s, 3 H), 3.63 (s, 3 H), 6.35–6.47 (m, 7 H), 6.52–6.55 (m, 3 H), 6.62–6.72 (m, 7 H), 6.79–6.89 (m, 9 H), 6.91–6.95 (m, 4 H), 7.13 (t, J = 7.7 Hz, 2 H), 7.58 (dd, J = 8.2 Hz, 1 H), 7.89–8.08 (m, 7 H).

B3. Prepared from *N*-phenylpyren-1-amine and **7** as described above for **B1**. Yield: 71%. Yellow solid. MS (FAB): *m*/*z*: 943.2 (M + H). Anal. Calcd. for $C_{70}H_{55}NO_2$: C, 89.23; H, 5.88; N, 1.49. Found: C, 89.01; H, 5.74; N, 1.38%. ^{1}H NMR ($CDCl_3$, δ): 1.10 (s, 9 H), 3.59 (s, 3 H), 3.60 (s, 3 H), 6.37–6.41 (m, 5 H), 6.58–6.62 (m, 3 H), 6.65–6.71 (m, 8 H), 6.76–6.86 (m, 8 H), 6.87–6.90 (m, 6 H), 7.07 (t, J = 7.7 Hz, 2 H), 7.52 (s, 1 H), 7.88–8.04 (m, 7 H).

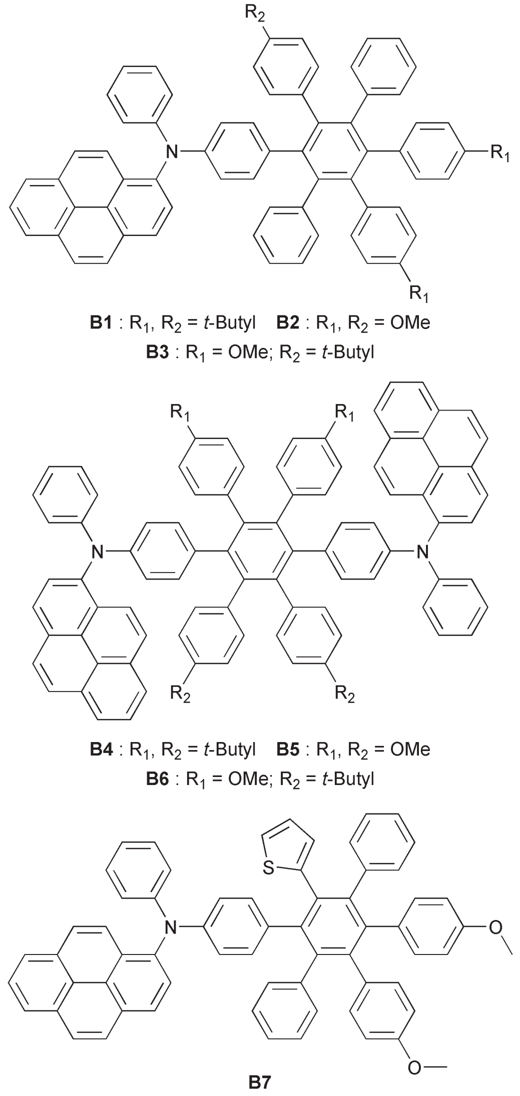


Chart 1 Structure of the amines.

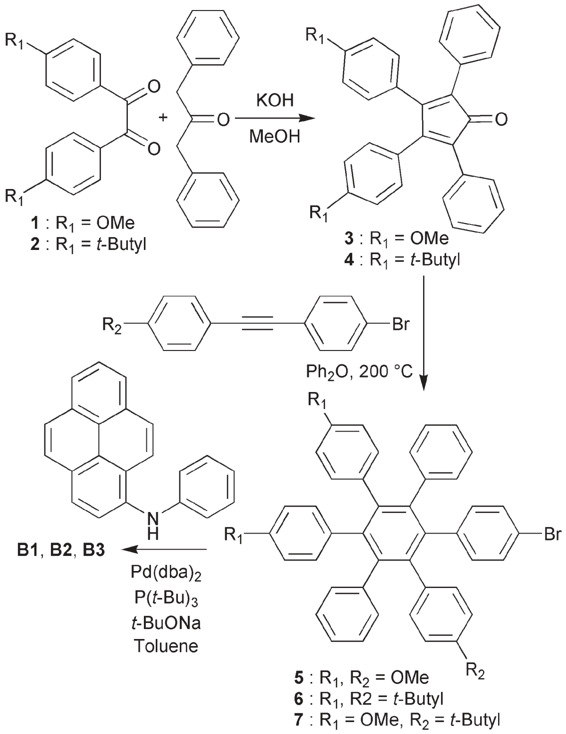
B4. Obtained in 89% yield from **10** and *N*-phenylpyren-1-amine (2.2 equiv.) as described above for **B1**. Yellow solid. MS (FAB): *m*/*z*: 1342.8 (M + H). Anal. Calcd. for $C_{102}H_{88}N_2$: C, 91.30; H, 6.61; N, 2.09. Found: C, 91.16; H, 6.52; N, 1.94%. ^{1}H NMR ($CDCl_3$, δ): 1.10 (s, 36 H), 6.57–6.72 (m, 20 H), 6.77–6.86 (m, 10 H), 7.03 (t, J = 7.8 Hz, 4 H), 7.56 (d, J = 8.2 Hz, 2 H), 7.80–7.83 (m, 2 H), 7.90–8.06 (m, 12 H), 8.10 (d, J = 7.3 Hz, 2 H).

B5. Synthesized from **11** as described above. Yield: 83%. Yellow solid. MS (FAB): *m*/*z*: 1238.5 (M + H). Anal. Calcd. for $C_{90}H_{64}N_2O_4$: C, 87.35; H, 5.21; N, 2.26. Found: C, 87.09; H, 5.18; N, 2.11%. ^{1}H NMR ($CDCl_3$, δ): 3.62 (s, 12 H), 6.45 (d, J = 8.5 Hz, 8 H), 6.58 (s, 8 H), 6.67–6.70 (m, 8 H), 6.79–6.88 (m, 5 H), 7.07–7.10 (t, J = 7.7 Hz, 4 H), 7.59 (d, J = 8.2 Hz, 2 H), 7.83–7.87 (m, 5 H), 7.96 (s, 2 H), 7.96–7.98 (m, 4 H), 8.03–8.12 (m, 6 H).

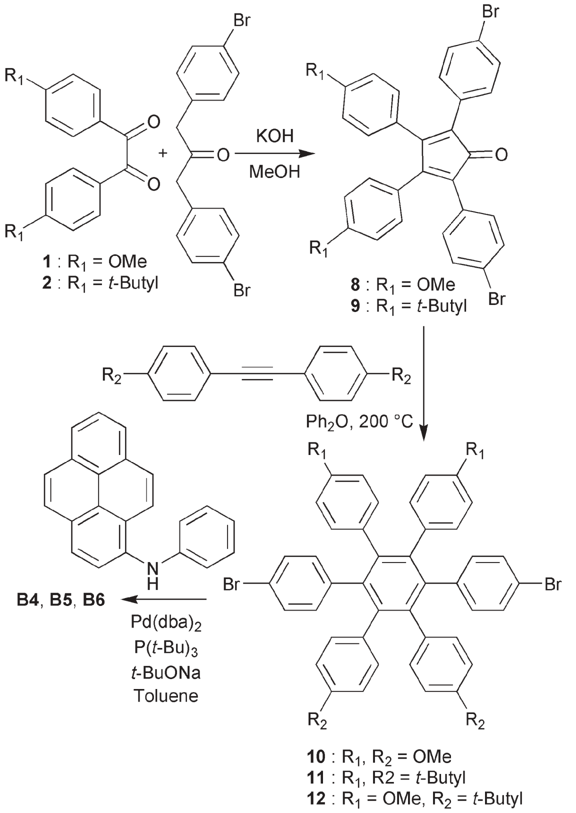
B6. Prepared from **12** as described above for **B4**. Yield: 71%. Yellow solid. MS (FAB): *m*/*z*: 1290.7 (M + H). Anal. Calcd. for $C_{96}H_{76}N_2O_2$: C, 89.41; H, 5.94; N, 2.17. Found: C, 89.26; H, 5.83; N, 1.99%. ^{1}H NMR ($CDCl_3$, δ): 1.14 (s, 18 H), 3.56 (s, 6 H), 6.43 (d, J = 8.6 Hz, 4 H), 6.59–6.62 (m, 8 H), 6.67–6.71 (m, 8 H), 6.75–6.80 (m, 4 H), 6.87 (d, J = 8.4 Hz, 6 H), 7.07 (t, J = 7.7 Hz, 4 H), 7.58 (d, J = 8.2 Hz, 2 H), 7.82–7.97 (m, 10 H), 8.01 (s, 2 H), 8.06–8.12 (m, 4 H).

Results and discussion

The synthetic pathways used for the construction of the blue-emitting chromophores are presented in Schemes 1 and 2. These involve three reactions, namely: (i) cycloaddition of a



Scheme 1 Synthesis of the monoamines, **B1–B3**.



Scheme 2 Synthesis of the diamines, **B4–B6**.

diarylated acetone with the corresponding α,β-diketone; (ii) Diels–Alder reaction between the cyclopentadienone formed in the previous reaction and an acetylene derivative; (iii) finally the C–N coupling reaction[20] of the bromo derivative of the hexaphenylbenzene and *N*-phenylpyren-1-ylamine. As most of the above mentioned reactions proceed with large conversion rates, the desired final products (**B1**–**B6**) were obtained in excellent yields. The compounds are yellow in colour and soluble in most common organic solvents such as dichloromethane, toluene, tetrahydrofuran, *etc.* and insoluble in alcohols. The NMR spectral data recorded in $CDCl_3$, mass spectral data and elemental analyses results are in accordance with the proposed structures.

Fig. 1 shows representative examples of the absorption and emission profiles of the compounds recorded in dichloromethane. All the relevant parameters are collected in Table 1. In the absorption spectra all the compounds display three prominent bands with unsymmetrical shape and adjoining shoulders. The most bathochromically shifted transition is ascribed to that originating from the amine to pyrene charge transfer state. On increasing the number of pyrenylamines present in the molecule the optical density of all the transitions increases significantly. This clearly indicates that most of the transitions are associated with the pyrenylamine unit. In comparison with the UV profile of similar compounds we assign the transitions at *ca.* 325 nm to that arising from the pyrene based π–π* transitions.[21] The intense bands appearing at *ca.* 250–280 nm probably stem from terphenyl chromophoric axes present in the molecule.[22] In fact there are three different terphenyl axes locatable in a single molecule which accounts for the multiple shoulders protruding in the higher energy region.

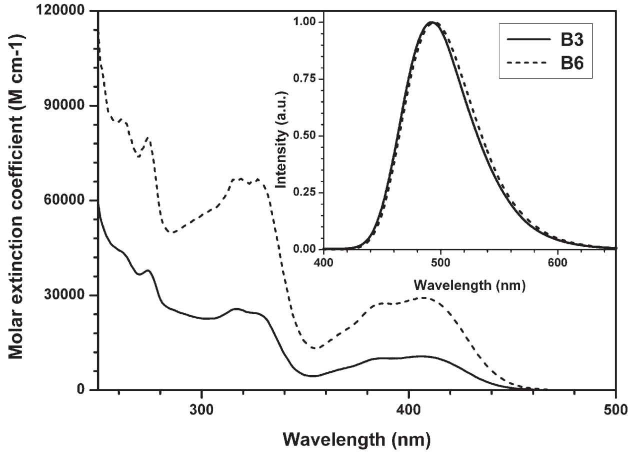


Fig. 1 Absorption and emission spectra of selected compounds (**B3** and **B6**) recorded in dichloromethane solution.

All the compounds exhibit identical emission profiles in dichloromethane solutions. This clearly indicates that the emission originates from a similar excited state in this class of compounds. Molecular modelling calculations (SPARTAN, PM3) reveal that in this series of compounds the HOMO is located in the aminopyrene segment while the LUMO is contributed by the pyrene unit. Evidently the amine to pyrene charge transfer state is the excited state in this series of compounds which will be somewhat polar in nature. Due to this a strong medium effect is observed in the fluorescence spectra of the compounds (**B1**–**B6**). For instance **B2** displays a blue-shifted emission profile in solid film (466 nm) when compared to that observed for dichloromethane solution (494 nm). This latter observation suggests that the polarity

Table 1 Physical parameters of the compounds[a]

Compd	λ_{max}/nm	λ_{em}/nm [Φ_F (%)]	λ_{em}(film)/nm	T_g, T_m, T_d/ °C	E_{ox}, ΔE_p/mV	HOMO/eV	LUMO/eV
B1	405, 388, 317, 274	494 [27]	474	141, 272, 449	386, 70	5.186	2.429
B2	406, 388, 317, 274	494 [51]	466	140, 268, 386	389, 73	5.189	2.369
B3	406, 387, 317, 274	494 [49]	470	140, 240, 456	391, 69	5.191	2.403
B4	406, 389, 326, 318, 274	492 [43]	488	157, 313, 535	381, 94	5.181	2.393
B5	406, 387, 328, 318, 274	492 [58]	476	155, 308, 512	405, 97	5.205	2.417
B6	406, 387, 327, 319, 274	492 [48]	490	151, 333, 540	389, 97	5.189	2.369

[a] Absorption and emission spectra of the compounds were recorded in dichloromethane solutions. Potentials reported are referenced related to the ferrocene internal standard. HOMO values were deduced from the relation: HOMO = 4.8 + E_{ox}. LUMO values were back calculated from the relation band gap = HOMO − LUMO where the band gap values were input from those derived from the optical edge.

of the solid film is less than that in the dichloromethane solution. This may be due to the reduced coplanarity of the molecules in the solid state due to the more restricted bond rotation.

Thermal properties of the compounds were investigated by differential scanning calorimetry and thermogravimetry under a flow of N_2. The glass transition temperatures and the thermal decomposition onset temperatures are listed in Table 1. These new giant molecules display impressive thermal stability and amorphous propensity. The glass transition temperatures (T_g) of the present compounds are significantly higher than those reported for commonly employed hole-transporting materials such as TPD (T_g = 60 °C) and α-NPD (T_g = 96 °C).[23] Also, the T_g of the present compounds are higher than those of hexathienyllbenzene derivatives containing six peripheral amines[24] and diamines based on biphenyl bridges.[23] The high T_g recorded for these compounds is attributed to the presence of the rigid pyrene segment and hexaphenylbenzene core in the molecular architecture.

The redox propensity of the materials is a very crucial factor that affects the performance of the OLEDs fabricated using them, as it will exert a direct impact on the charge injection and mobility in the molecular layer.[25] We have examined the redox behaviour of the present compounds by the cyclic voltammetric method. All the molecules underwent a quasi-reversible one-electron oxidation originating from the pyrenylamine segment. No reduction waves were noticed within the observable potential window.

HOMO values calculated from the oxidation potentials by comparing with the ionization potential of ferrocene (HOMO = 4.8 − E_{ox}; where E_{ox} is the oxidation potential of the material with referene to ferrocene) and the LUMO values deduced from the band gap calculated from the optical edge are listed in Table 1. The orbital energy values are favorable for charge injection and transport in a multi-layered OLED configuration. The closeness of the HOMO of these materials to the work function of ITO (E_f = 4.7 eV) indicates that hole injection into the molecular layer of these compounds will be effective. Use of an appropriate electron transporting layer (ETL) is essential to restrict recombination inside the hole-transporting layer (HTL). This will ensure blue emission of the present compounds. Inspection of the energy level alignment for the molecules and electron transporting materials such as Alq_3 and TPBI depicted in Fig. 2 will help to decide on this issue. It is evident that the passage of holes from the compounds to TPBI will be retarded due to the large HOMO energy barrier (∼1.0 eV). However electrons can easily cross over to the HTL from TPBI as the LUMO barrier is small (∼0.3 eV) when compared to the HOMO barrier. However, use of Alq_3 as electron-transporting material affects both the HOMO and LUMO barriers at the HTL/ETL junction. It is also inferred that a ∼0.6 eV increase in the LUMO barrier and a ∼0.2 eV decrease in the HOMO barrier when compared to that of the HTL/TPBI interface will dramatically affect the positioning of the recombination zone in the Alq_3 based devices.

We have tested the both electron transporting materials TPBI and Alq_3 with the device structure ITO/**B1**–**B3** or **B7**/ETL/Mg:Ag. All the TPBI based devices led to bright blue emission while the Alq_3 devices produced intense green emission originating from Alq_3. The EL spectra of the TPBI based devices are narrow with small full-width at half-maxima values and were superimposable onto the PL spectra of the vapour deposited thin (approx. 80 nm) film. A representative EL and PL comparison is provided in Fig. 3 for the compound **B1**. Though the CIE 1931 x, y coordinates realized for these devices slightly deviate from the NTSC standard blue colour (CIE, x, y: 0.14, 0.08), they still lie in the pure blue region.

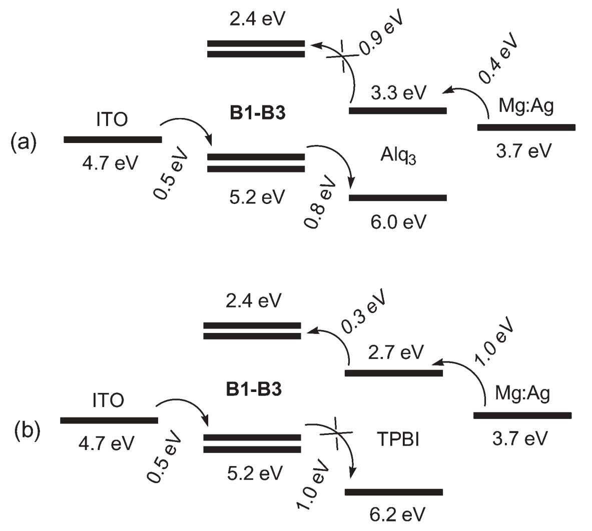


Fig. 2 Energy level alignment for the Alq_3 (a) and TPBI (b) based devices.

We believe the comparatively larger LUMO barrier (0.9 eV) at the interface of Alq_3/HTL, when compared to the barrier at the TPBI/HTL interface (∼0.3 eV), plays an important role by slowing down the electron injection into the HTL layer. As this happens the holes that are more mobile can easily surpass the HTL/Alq_3 HOMO barrier (∼0.8 eV) and leak into the Alq_3 layer. To restrict the recombination zone within the HTL in Alq_3 based devices we have introduced a thin (10 nm) hole blocking layer (HBL). Since the TPBI based devices yielded blue emission originating from the HTL, it can be safely assumed that the TPBI layer effectively blocks the holes in

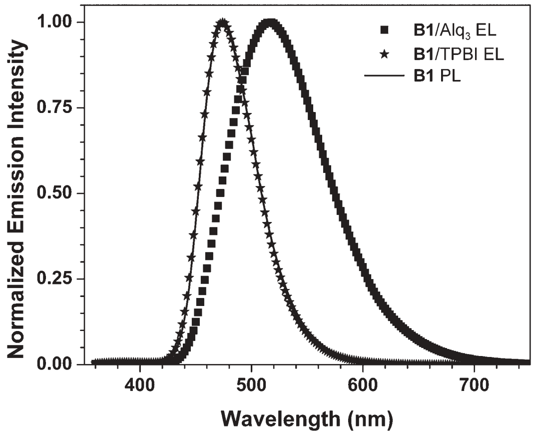


Fig. 3 Comparison of EL spectra observed for the **B1** based devices and PL spectra of the vapour deposited **B1** film.

Table 2 EL parameters for the devices fabricated using **B1**–**B3** and **B7**

Device	V_{ON}/V	L_{max}/cd m^{-2}	$\eta_{ex,max}$ (%)	λ_{EL} (fwhm)/nm	CIE 1931 *x*, *y*	L_{100}/ cd m^{-2}	$\eta_{ex,100}$ (%)	$\eta_{cu,100}$/ cd A^{-1}
ITO/**B1**/TPBI/Mg : Ag[a]	3.0	21150 at 14 V	2.7	474 (56)	0.13, 0.21	3750[c]	2.5[c]	3.8[c]
ITO/**B2**/TPBIMg : Ag[a]	3.5	10800 at 14 V	2.0	464 (54)	0.13, 0.15	2370[d]	2.0[d]	2.4[d]
ITO/**B2**/TPBI/Alq_3/Mg : Ag[b]	3.0	10170 at 15 V	1.7	468 (52)	0.13, 0.17	1720[e]	1.3[e]	1.7[e]
ITO/**B2**/TPOB/Alq_3/Mg : Ag[b]	3.5	11070 at 14.5 V	1.7	466 (52)	0.14, 0.16	2020[f]	1.7[f]	2.0[f]
ITO/**B3**/TPBI/Mg : Ag[a]	3.0	20590 at 14 V	2.6	472 (56)	0.13, 0.20	3520[g]	2.4[g]	3.5[g]
ITO/**B3**/TPBI/Alq_3/Mg : Ag[b]	3.5	16210 at 15 V	2.2	474 (58)	0.13, 0.22	3400[h]	2.2[h]	3.4[h]
ITO/**B3**/TPOB/Alq_3/Mg : Ag[b]	4.0	7820 at 15 V	1.4	476 (58)	0.13, 0.23	1940[i]	1.2[i]	1.9[i]
ITO/**B7**/TPBI/Mg : Ag[a]	3.5	11970 at 15 V	2.5	472 (54)	0.13, 0.20	2610[j]	1.8[j]	2.6[j]

[a] Device structure: ITO/compd (40 nm)/TPBI (40 nm)/Mg : Ag. [b] 40 nm HTL, 10 nm HBL and 30 nm ETL were used. [c] At 6.8 V. [d] At 7.7 V. [e] At 7.7 V. [f] At 8.2 V. [g] At 7.0 V. [h] At 8.7 V. [i] At 10.0 V. [j] At 6.5 V.

such architectures while permitting electron injection into HTL. So why not use TPBI as a HBL in Alq_3 based devices? Device engineering strategies using TPBI as a hole blocking host have been successfully demonstrated earlier to result performance enhancement and colour purity in blue emitting doped devices.[26] The compounds **B2** and **B3** were used to optimize the Alq_3 based devices further. Indeed the use of a thin layer of TPBI (10 nm) effectively blocked the holes and led to blue emission. Additionally we found that the use of a oxadiazole based star-burst electron-transporting material, TPOB,[27] also produced the same result for which the LUMO is located at 2.9 eV. Full details are collected in Table 2.

The *I*–*V*–*L* characteristics of the devices are displayed in Fig. 4 and 5 and the essential performance parameters are collected in Table 2. Generally, for the blue-emitting devices the use of a hole-blocker often led to an improvement in efficiency. In our cases we found that devices where TPBI was used as the electron-transporting layer excel in performance when compared to Alq_3 based devices containing an additional hole blocking layer. This clearly suggests that the electron injection into the emissive HTL is the limiting factor. The performance of the blue-emitting devices fabricated using **B1** or **B3** and TPBI as electron-transporting layer rivals certain anthracene[11,28] based blue-emitting materials and amine-oxadiazole[29] conjugates reported earlier. It is to be noted here that fluorene based blue-emitting materials were found to facilitate electron injection from the metal cathode thus leading to superior performance in organic light-emitting diodes.[30]

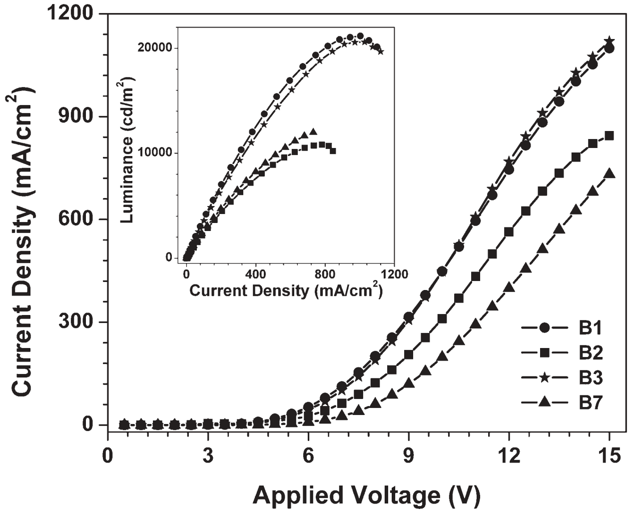


Fig. 4 *I*–*V*–*L* characteristics of the TPBI based devices of **B1**–**B3** and **B7**.

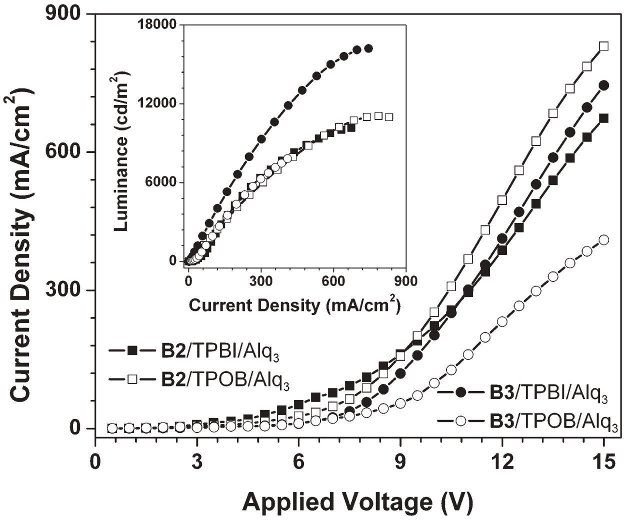


Fig. 5 *I*–*V*–*L* characteristics of Alq_3 based devices of **B2** and **B3** with an additional hole-blocking layer.

In conclusion, we have synthesized a new series of pyrene-amines that contain hexaphenylbenzene chromophores. The design leads to high T_g blue-emitting materials possessing good hole transporting capability. Bright blue emitting devices were realized for both TPBI and Alq_3 based devices, while the latter OLEDs required a thin hole-blocking layer to achieve recombination inside the hole transporting layer. The new materials described here represent a novel entry to the blue-emitting OLEDs that may find potential application in the fabrication of white OLEDs or as hosts in electrophosphorescent devices.

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