Hyperbranched Poly(arylene ethynylene)s with Triphenylamine Core for Polymer Light-Emitting Diodes

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ABSTRACT: A series of light-emitting hyperbranched poly(arylene ethynylene)s (HB-PAEs) were prepared by the Sonogashira coupling from bisethynyl of carbazole, fluorene, or dialkoxybenzenes (A₂ type) and tris(4-iodophenyl)amine (B3 type). For comparison, two linear polymers (L-PAEs) of the HB analogs were also synthesized. The polymers were characterized by Fourier transform infrared, NMR, and GPC. The HB polymers showed excellent solubility in chloroform, THF, and chlorobenzene when compared with their linear analogs. The number-average molecular weight (M_n) of the polymers determined from GPC was found to be in the range of 18,600-34,200. The polymers were thermally stable up to 298-330 °C with only 5% weight loss. The absorption maxima of the polymers were between 354 and 411 nm with optical band gap in the range of 2.5-2.9 eV. The HB polymers were found to be highly fluorescent with photoluminescence quantum yields

INTRODUCTION Conjugated polymers have attracted lot of interest in scientific and technological fields because of their potential use as semiconductor and electroactive materials in a variety of optoelectronic devices, such as organic light-emitting diodes (OLEDs),¹ field effect transistors,² photovoltaic cells,³ nonlinear optical devices,⁴ and electrochromic cells.⁵ In particular, OLEDs using conjugated polymers have drawn great attention because of easy processing, low operating voltages, faster response times, and facile color tuning over the full visible range, which makes them suitable for large-area flat panel display.⁶ Therefore, designing new polymeric materials with varied optoelectronic properties is of the great choice to meet the requirements for the next generation of display technology.

Among conjugated polymers, poly(arylene ethynylene)s (PAEs) have unique properties such as photoluminescence,⁷ nonlinear optics,⁸ and exceptionally high-solution state PL efficiencies⁹ in comparison to other conjugated polymers. Such properties render these materials as another class of prospective materials for various optoelectronic applications.

around 33–42%. The highest occupied molecular orbital energy levels of the polymers calculated from onset oxidation potentials were found to be in the range from –5.83 to –6.20 eV. Electroluminescence (EL) properties of three HB-PAEs and one L-PAE were investigated with device configuration ITO/ PEDOT:PSS/Polymer/LiF/AI. The EL maxima of HB-PAEs were found to be in the range of 507–558 nm with turn-on voltages around 7.5–10 V and maximum brightness values of 316–490 cd/m². At the same time, linear analog of one HB-PAE was found to show a maximum brightness of 300 cd/m² at a turn-on voltage of 8.2 V. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 832–841, 2011

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Although several PAEs were developed till date and widely used as sensory materials,¹⁰ little effort has been paid to PAEs as potential OLED materials.¹¹ This is because of the reduced emission efficiencies in the solid state, which has been attributed to the formation of the aggregates.¹² Besides, the alkyne units in PAEs limit the redox properties of polymers resulting in a large potential barrier to the injection and transportation of holes.¹³ Hence, to use PAEs as efficient OLED materials, one has to design the structure to minimize the aggregation and enhance the charge-balancing properties. One of the plausible solutions is to make hyperbranched poly(arylene ethynylene) (HB-PAEs) with suitable choice of the comonomers. HB polymers show good solubility, better processibility, and more tunable emission color than linear polymers.¹⁴ In addition, the HB polymers can improve the morphologies of the thin films and prevent crystallization.¹⁵ Moreover, their three-dimensional (3D) structures help in reducing the aggregation of the conjugated polymer chains and in some cases, it improves their emission efficiency and thermal stability.16

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Herein we report a series of PAEs with HB architecture synthesized via $A_2 + B_3$ approach. Several electron-donating aromatic units have been introduced in the polymer backbone with triphenylamine (TPA) as the core. Particular attention was paid to the TPA moieties because of their ability for the hole injection.¹⁷ TPA derivatives can be viewed as 3D systems, and amorphous character of these materials offers possibilities to develop active materials for OLEDs. On the other hand, ethynylene units in the polymeric backbone would provide an enhanced π -electron delocalization because of the coplanar molecular structure. Hence, better charge-balancing properties would be expected from these set of polymers.

We investigated thermal, electrochemical, and optoelectronic properties of resulting polymers. The resultant polymers have high molecular weights and high thermal stability and can be used for OLEDs. The polymer light-emitting devices (PLEDs) based on HB-PAE1, HB-PAE2, HB-PAE4, and L-PAE2 were fabricated and evaluated to investigate the light-emitting properties.

EXPERIMENTAL

Materials

Anhydrous chlorobenzene was purchased from Sigma-Aldrich. Diisopripylamine was dried over sodium ketyl radical. 9-(2-Ethylhexyl)-3,6-diethynyl-9*H*-carbazole (**1**), 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9*H*-fluorene (**2**), 1-(2-ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**3**), 4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**4**), and 4-iodo-*N*-(4-iodophenyl)-*N*-phenylaniline (**6**) were synthesized following the literature procedure.¹⁸

Measurements

Thin layer chromatography was performed with Merck silica gel 60 F254 aluminum sheets. Chromatographic separations were carried out using Merck silica gel 100-200 mesh. Fourier transform infrared (FTIR) spectra were obtained from a Nicolet 5700 FTIR spectrophotometer. ¹H NMR spectra were recorded using either a Brucker 500 or 300 MHz FT-NMR spectrometer with chloroform-d as solvent. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Molecular weights were determined by GPC on Waters 2690 separations module apparatus using a Waters 2410 refractive index detector. All the measurements were carried out at 35 °C using THF as solvent and polystyrene as standard. UV-vis and PL spectra were recorded using Varian Carry 5000 scan and Spex Flurolog-3-11 spectrometers. Thermogravimetric analysis (TGA; Hi Res TGA 2950, TA Instruments) of the samples was carried out at a heating rate of 10 $\,^\circ\text{C/min}$ under nitrogen atmosphere. Differential scanning calorimetric (DSC) measurements of the polymers were performed under nitrogen at a heating and cooling rate of 5 °C/min with a TA DSC Q100 instrument. Cyclic voltammetry (CV) was performed on an AUTOLAB/PGSTAT30 potentiostat with a three-electrode cell in a solution of Et_4NBF_4 (0.10 M) in acetonitrile at a sweep rate of 50 mV/s. Platinum electrode coated with polymer film was used as working electrode. Platinum mesh electrode was used as counter electrode and Ag/Ag⁺ electrode was used as reference. The measurements were calibrated using ferrocene as

standard. PLED devices were fabricated with ITO as a positive electrode, LiF/Al as a negative electrode and the film of the polymer between them as emissive layer. The device configuration was ITO/PEDOT:PSS/HB-PAE/LiF/Al structure. Active area of all fabricated devices was $4 \times 4 \text{ mm}^2$ and all electrical measurements were performed under ambient condition without encapsulation. Electroluminescence (EL) spectra of the devices were obtained using HR 2000 Ocean Optics spectrometer, having a CCD array and fiber optic probe. The current–voltage and luminescence–voltage characteristics were studied using Keithley 617 electrometer and luminance meter (LMT L1009).

Synthesis

Tri(4-iodophenyl)amine) (5)

TPA (3 g, 12.24 mmol), potassium iodate (2.88 g, 13.47 mmol), and acetic acid (100 mL) were added to a 250-mL round-bottom flask. To the mixture, potassium iodide (4.47 g, 26.93 mmol) was added while stirring. The mixture was heated at 80 °C for 12 h. The reaction mixture was cooled and the precipitate formed was collected by filtration. The residue was thoroughly washed with water till neutral. The solid was dissolved in chloroform (100 mL) and consecutively washed with water and NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to obtain light gray solid. Purifications by column chromatography (silica gel) using petroleum ether as eluent isolated the compound as an off white solid. Yield: 87%. M.P.: 167 °C. ¹H NMR and ¹³C NMR data were well matched with literature values.¹⁹

General Method for Polymerization (for HB-PAE and L-PAE)

Under nitrogen atmosphere, anhydrous chlorobenzene (4 mL) and diisopropylamine (2 mL) were added by syringe into a thoroughly dried 25-mL Schlenk flask charged with tris(4-iodophenyl)amine (5) (100 mg, 0.16 mmol), (PPh₃)₂PdCl₂ (2.24 mg, 0.0032 mmol), and CuI (1.22 mg, 0.0064 mmol). To the stirring mixture, bisethynylene monomer (1, 2, 3, or 4; 0.24 mmol) in chlorobenzene (2 mL) was added dropwise by syringe. The mixture was stirred for 72 h at room temperature and excess bromobenzene was added. The solution was stirred for additional 6 h and poured into methanol (50 mL). The precipitate was filtered and dried under vacuum to obtain the polymer as yellow powder. The polymer was stored in desiccators in absence of light for further use.

Similar procedure was adopted for synthesizing the linear polymers. In this case, equimolar amount of 4-iodo-N-(4-iodophenyl)-N-phenylaniline (**6**) and bisethynylene monomer (**1** or **2**) were taken for polymerization.

HB-PAE1

9-(2-Ethylhexyl)-3,6-diethynyl-9*H*-carbazole (**1**) (78.48 mg, 0.24 mmol) was used. Yield: 82%. FTIR (cm⁻¹, KBr): 2954, 2926, 2868, 2360, 2338, 1597, 1505, 1481, 1315, 1281, 805. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 8.22 (Ar-H, Carbazole), 7.56 (Ar-H, Carbazole), 7.46 (Ar-H, Carbazole), 7.04 (Ar-H, TPA), 6.84 (Ar-H, TPA), 4.12 (NCH₂), 2.00 (CH), 1.55–1.27 (CH₂), 0.85 (CH₃). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 146.55, 141.44, 131.58, 129.47, 126.03, 123.95, 121.61,

119.90, 116.56, 111.20, 94.65, 85.59, 35.20, 33.52, 28.09, 26.92, 22.66, 14.03, 13.95, 10.53. $M_{\rm n}=$ 19,000, $M_{\rm w}/M_{\rm n}=$ 2.4 (GPC, polystyrene calibration). $T_{\rm d}$ (°C, 5% weight loss): 330.

HB-PAE2

9,9-Bis(2-ethylhexyl)-2,7-diethynyl-9*H*-fluorene (**2**) (105.68 mg, 0.24 mmol) was used. Yield: 86%. FTIR (cm⁻¹, KBr): 2954, 2923, 2858, 2361, 2335, 1540, 1514, 1457, 820. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 7.65 (Ar-H, fluorene), 7.54 (Ar-H, fluorene), 7.07 (Ar-H, TPA), 6.86 (Ar-H, TPA), 2.17 (CH₂), 2.00 (CH), 1.66–0.74 (CH₂), 0.55 (CH₃). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 150.91, 146.55, 138.44, 132.74, 131.58, 130.47, 128.04, 127.00, 126.33, 123.35, 121.61, 120.12, 119.90, 94.15, 84.80, 44.54, 34.68, 33.52, 27.99, 26.92, 22.66, 14.03, 13.95, 10.23. $M_n = 22,700$, $M_w/M_n = 3.3$ (GPC, polystyrene calibration). T_d (°C, 5% weight loss): 325.

HB-PAE3

1-(2-Ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (3) (68.25 mg, 0.24 mmol) was used. Yield: 80%. FTIR (cm⁻¹, KBr): 2954, 2925, 2862, 2361, 2335, 1592, 1507, 1488, 1316, 1280, 1215, 1034, 828. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 7.56 (Ar-H), 7.43 (Ar-H), 7.00 (Ar-H, TPA), 6.86 (Ar-H, TPA), 4.56–3.69 (OCH₂), 3.22 (OMe), 1.79 (CH), 1.56–1.35 (CH₂), 0.96 (CH₃). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 152.40, 150.91, 146.45, 131.58, 121.61, 119.12, 118.90, 117.60, 112.76, 95.15, 83.90, 70.23, 54.68, 33.56, 28.00, 26.93, 22.76, 14.03, 13.85, 10.21. $M_{\rm n} = 18,600, M_{\rm w}/M_{\rm n} = 2.9$ (GPC, polystyrene calibration). $T_{\rm d}$ (°C, 5% weight loss): 302.

HB-PAE4

4-Bis(2-ethylhexyloxy)-2,5-diethynylbenzene (4) (91.82 mg, 0.24 mmol) was used. Yield: 84%. FTIR (cm⁻¹, KBr): 2955, 2926, 2862, 2361, 2335, 1509, 1487, 1316, 1271, 829. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 7.54 (Ar-H), 7.02 (Ar-H, TPA), 6.85 (Ar-H, TPA), 4.46–3.65 (OCH₂), 1.79 (CH), 1.56–1.35 (CH₂), 0.96 (CH₃). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 151.48, 146.05, 131.58, 122.61, 118.90, 117.60, 112.56, 95.95, 83.90, 72.23, 41.68, 32.56, 28.96, 23.93, 22.76, 13.85, 11.21. $M_n = 19,500$, $M_w/M_n = 3.4$ (GPC, polystyrene calibration). T_d (°C, 5% weight loss): 298.

L-PAE2

4-Iodo-*N*-(4-iodophenyl)-*N*-phenylaniline (6) (100 mg, 0.20 mmol) and 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9*H*-fluorene (2) (88.13 mg, 0.20 mmol) were used. Yield: 79%. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 7.67 (Ar-H, fluorene), 7.54 (Ar-H, fluorene), 7.48 (Ar-H, fluorene), 7.36 (Ar-H, TPA), 7.19 (Ar-H, TPA), 7.12 (Ar-H, TPA), 6.93, 6.86 (Ar-H, TPA), 2.08 (CH₂), 1.58 (CH), 1.26–0.74 (CH₂), 0.55 (CH₃). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 150.94, 147.11, 138.24, 132.60, 129.52, 126.07, 125.39, 125.11, 124.00, 123.35, 122.94, 119.76, 44.54, 34.62, 33.51, 27.98, 26.98, 22.67, 14.03, 10.29. M_n = 34,200, M_w/M_n = 3.8 (GPC, polystyrene calibration). T_d (°C, 5% weight loss): 314.

RESULTS AND DISCUSSION

Synthesis and Characterization

The HB polymers were synthesized by $A_2 + B_3$ approch using Sonagashira polycondensation reaction. In this method,

3:2 molar ratio of the bis-ethynyl monomer (1, 2, 3, or 4) and tri(4-iodophenyl)amine) (5) were allowed to react in presence of catalytic amount of (PPh₃)₂PdCl₂ and CuI as shown in Scheme 1. Initially, the polymerization was carried out following the procedure routinely used for the synthesis of linear PAEs.^{20,11a} In this procedure, A₂ (0.24 mmol) and B₃ (0.16 mmol) monomers were dissolved in chlorobenzene (4 mL) to which (PPh₃)₂PdCl₂ (0.0032 mmol), CuI (0.0064 mmol), and diisopropylamine (2 mL) were added and the mixture was heated under stirring at 65 °C. However, in this condition, the reaction mixture gelled within 30 min. Therefore, to avoid gelation, the polymerization was carried out by taking the B₃ monomer along with catalyst and base and a chlorobenzene solution of A2 was added slowly. For all the polymerization, chlorobenzene was used as solvent for polymerization to obtain high molecular weight as well as more soluble polymers.¹⁸ It was observed that by increasing the reaction temperature above 50 °C, the color of the reaction mixture turned dark brown with the formation of insoluble mass. Therefore, all the polymerization reactions were carried out at room temperature. It was also observed that the soluble polymers without end capping are found to become insoluble after Soxhlet extraction and drying. This dark color and insolubility of the polymers may be attributed to crosslinking of the polymers. This type of behavior was also observed by others and described the crosslinking of the polymers due to the tendency of cyclo- and [4 + 2] cyclodimerization of the remaining ethynyl groups with ene-ethynyl moieties in the presence of Pd traces or possible Bergman cyclization of the ene-dievne moieties in the polymer.²¹

To compare with the linear analog, two linear polymers were synthesized as shown in Scheme 1 (part 2). The polymerizations were carried out by reacting equimolar ratio of 4-iodo-N-(4-iodophenyl)-N-phenylaniline (6) and bisethynylene monomers (1 or 2) in similar conditions as for HB polymers. After the successive polymerization and end capping, it was found that the fluorene-containing polymer (L-PAE2) was soluble in most of the organic solvents where as the carbazole-containing polymer (L-PAE1) was insoluble. This could be because of the more rigid structure of the linear PAEs when compared with its HB analog. The higher solubility of L-PAE2 when compared with L-PAE1 is because of the presence of two 2-ethylhexyl group which enhances the solubility. As L-PAE1 was insoluble, no characterizations of the polymer could carry out.

The number-average molecular weights (M_n) of the polymers estimated by GPC were in the range of 18,600–34,200 with polydispersity index of 2.4–3.8. The yield and molecular weights of the polymers are summarized in Table 1. In HB polymer series, the polymers HB-PAE2 and HB-PAE4 had higher molecular weight when compared with HB-PAE1 and HB-PAE3. This could be attributed to the presence of the two 2-ethylhexyl groups which enhance the solubility. However, comparing with the HB polymers, the linear polymer was found to possess much higher molecular weight in GPC probably because of larger hydrodynamic volume. All the synthesized polymers were analyzed by FTIR and ¹H NMR





Part 2



(i) (PPh₃)₂PdCl₂, CuI, Diisopropylamine, Chlorobenzene, rt

SCHEME 1 Synthesis of polymers.

spectroscopy. In IR spectra, the presence of two bands (due to Fermi resonance) around 2300 cm⁻¹ assignable to disubstituted ethynylene moiety at the main chain and the absence of absorption peaks attributed to monosubstituted ethynylenes (C—H stretching vibration around 3300 cm⁻¹ and C=C stretching vibration around 2100 cm⁻¹) support the formation of polymers. The ¹H NMR spectra of a representative polymer HB-PAE1 is shown in Figure 1. In ¹H NMR spectra, the aromatic protons show broader resonance peak ranging from 8.25 to 6.85 ppm (peaks have been assigned in

Fig. 1) because of the possible aggregation of polymer in solution. The signal of the methylene group adjacent to N-atom appears around 4 ppm. For all polymers, the characteristic resonance peaks of 2-ethylhexyl chains appear in the range 2.20–0.57 ppm. The absence of terminal acetylene proton in ¹H NMR spectra indicated that the end-capping reaction was completed. Because of the unavailability of distinguishable dendritic, linear and terminal signals in ¹H NMR spectra, the degree of branching of the polymers could not determined.²² To confirm the HB structure, ¹³C NMR analysis of both linear

 TABLE 1 Molecular Weight Distribution and Thermal Stability of Polymers

Polymer	Yield (%)	<i>M</i> _n ^a	PDI (M_w/M_n)	<i>T</i> _d (°C)
HB-PAE1	82	19,000	2.4	301 ^b (330) ^c
HB-PAE2	86	22,700	3.3	287 ^b (325) ^c
HB-PAE3	80	18,600	2.9	260 ^b (302) ^c
HB-PAE4	84	19,500	3.4	263 ^b (298) ^c
L-PAE2	79	34,200	3.8	270 ^b (314) ^c

^a Determined by GPC relative to polystyrene standards.

^b Temperature at 2% weight loss.

^c Temperature at 5% weight loss.

and HB polymers were performed and were compared side by side. In ¹³C spectra, the peak at 125.39 ppm assigned to the unsubstituted phenyl ring in triphenyl amine core indicated the formation of linear polymer (L-PAE2) where as the absence of that peak confirmed the formation). Additionally, two peaks at 147.11 ppm for linear polymer (L-PAE2) assigned to three carbon atoms attached to N-atom of TPA indicate the formation of linear polymer where as a single peak at 146.55 ppm for HB-PAE2 assigned to three carbon atoms attached to three carbon atoms attached to N-atom of TPA confirmed the formation of HB polymer (Figs. S1 and S2, Supporting Information of HB polymer (Figs. S1 and S2, Supporting Information of HB polymer (Figs. S1 and S2, Supporting Information, indicated by arrow).

Optical Properties

As the optical spectra are usually indicative of the structural features of conjugated polymers, the properties of these new



FIGURE 2 UV-vis absorption spectra of polymers in dilute $CHCl_3$ solution.

polymers were studied by UV-vis and PL spectroscopies. The UV-vis spectra of all the polymers were recorded in solution as well as in thin film. Figure 2 shows the normalized UV-vis spectra of polymers measured in THF. The absorption maxima of the solutions are summarized in Table 2. The HB polymers showed solution absorption maxima in the wavelength region between 353 and 418 nm where as the linear polymer L-PAE2 showed absorption maxima at 388 nm. The



FIGURE 1 ¹H NMR spectrum of HB-PAE1 in CDCI₃.

	Solution (Optical)		Thin Film (Optical)			Oxidation (Electrochemical)			
Polymer	Abs λ_{max} (nm)	PL λ_{max} (nm)	Abs λ _{max} (nm)	PL λ _{max} (nm)	Φ _{PL} (%)	E _g (eV)ª	E _{onset} (V)	HOMO (eV) ^b	LUMO (eV) ^c
HB-PAE1	353	434	354	435, 483	33	2.91	1.03	-5.83	-2.92
HB-PAE2	374	438	375	471, 507	42	2.66	1.20	-6.00	-3.34
HB-PAE3	408	469	410	540	36	2.58	1.36	-6.16	-3.58
HB-PAE4	411	473	411	545	39	2.53	1.40	-6.20	-3.67
L-PAE2	388	442	401	508	30	2.80	1.10	-5.90	-3.10

TABLE 2 Optoelectronic Properties of the Polymers

^a Optical band gap.

^b Calculated from onset oxidation potential.

absorption peak of L-PAE2 is red shifted 14 nm relative to that of HB-PAE2, which is attributed to its longer effective conjugation length because of higher molecular weight. Normalized thin film absorption spectra of the polymers are depicted in Figure 3 and the corresponding optical data are given in Table 2. The absorption maxima of the HB polymer thin films occur between 354 and 411 nm where as for linear L-PAE2, absorption maxima occur at 401 nm. It is important to note that in the absorption spectra, red shift of L-PAE2 (13 nm) in going from solution to film state is higher than that of HB-PAE2 (01 nm). This is attributed to higher interchain interaction in L-PAE2, which is facilitated by its linear structure. However, the smaller red shift of HB-PAE2 is mainly because of its globular structure.²³ The onset of the thin film absorption spectra were used to determine the band gap of the polymers. The calculated band gaps of polymers are in the range of 2.5-2.9 eV and are summarized in Table 2.

The PL spectra of all the polymers were also recorded in THF solution as well as in film. The emission maxima of the



FIGURE 3 UV-vis absorption spectra of polymer thin films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^c Calculated from the HOMO energy level and the optical band gap.

solutions and thin films are summarized in Table 2. The maxima of emission in solution are centered around 434-473 nm (Fig. 4). While comparing the emission maxima with the polymeric structure, it was observed that the alkoxyphenyl-containing polymers (HB-PAE3 and HB-PAE4) showed a bathochromic shift when compared with the others (HB-PAEP1 and HB-PAE2). This indicates the better packing of the polymeric main chain in case of HB-PAE3 and HB-PAE4 when compared with rest of the HB polymers. This could be because of the formation of symmetric acetylene linkage between the TPA unit and the alkoxyphenyl units which helps the polymer chains for better packing. The PL emission in thin film of HB-PAEs and L-PAE2 shows the emission maxima between 435 and 545 nm (Fig. 5). Compared with solution emission, the PL emission of the polymer films shows a red shift, probably because of the aggregation of the polymer chains in the solid state. The PL spectra of L-PAE2 was found to be red shifted both in solid and in solution state as compared the HB analog HB-PAE2 probably due to the better packing of the former polymeric main chain. Fluorescence



FIGURE 4 PL spectra of the studied polymers in dilute CHCl₃ solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 PL spectra of the polymer thin films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quantum yield (Φ_{PL}) of the polymers was determined following our earlier reported procedure²⁴ and the results are summarized in Table 2. A moderately PL quantum yield was obtained from all HB polymers where as a weak PL quantum yield was obtained for L-PAE2. The low PL quantum yield of L-PAE2 could be because of its more aggregation nature thereby quenching the PL quantum yield. Compared with TPA-carbazole copolymer HB-PAE1, TPA-fluorene copolymer HB-PAE2 had higher quantum yield. The introduction of carbazole units into TPA polymers reduces the quantum yield of emission.



FIGURE 6 TGA traces of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties

The thermal properties of the synthesized polymers were investigated using TGA and DSC. The carbazole-containing HB polymer HB-PAE1 was the most stable one among these polymers, which shows 2% decomposition at 300 °C under nitrogen (Fig. 6). This can be attributed to the presence of additional nitrogen atom in the polymer. The other polymers HB-PAE2, HB-PAE3, and HB-PAE4 show 2% weight loss at 287, 260, and 268 °C, respectively. The L-PAE2 shows 2% weight loss at 270 °C. DSC analysis of the polymer indicated



FIGURE 7 Cyclic voltammograms of the polymers.



FIGURE 8 Electroluminescence spectra of the studied polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the absence of glass transition in the range of 0–200 °C. However, because of the very rigid nature of these polymers, the possibility of a glass transition temperature higher than 200 °C cannot be completely excluded. In all cases, no crystallizing and melting peaks were detected, suggesting that these polymers are amorphous.²⁵

Electrochemical Properties

To investigate the energy levels of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the electrochemical properties of polymers were investigated by CV. The measurements were calibrated using ferrocene as the standard. The results of electrochemical measurements are listed in Table 2. Figure 7 shows the oxidation waves of the polymers as a result of the *p*-type doping. The polymers exhibit irreversible *p*-doping/dedoping(oxidation/rereduction) processes at positive potentials with onset of potentials between 1.03 and 1.40 V versus Ag/Ag⁺. Among the four HB polymers, HB-PAE1 possesses the lowest onset oxidation potential and HB-PAE4 possesses the highest onset oxidation potential. This could be because of the better electron-donating properties of carbazole (in HB-PAE1) and fluorene (in HB-PAE2) moieties when compared with the dialkoxy phenyl units (in HB-PAE3 and HB-PAE4). The onset oxidation potential of linear polymer (L-PAE2) was found to be 1.10 V. From the onset oxidation potentials, the HOMO energy levels of the polymers were calculated according to the equation: HOMO [ionization potential (IP)] = $-e(E_{ox} + 4.8 \text{ eV})$, assuming that the IP of ferrocene is -4.8 eV for the Fc/Fc⁺ system.²⁶ The HOMO energy levels of the HB polymers were found to be in the order: HB-PAE4 (-6.20 eV) < HB-PAE3 (-6.16 eV) < HB-PAE2(-6.00 eV) < HB-PAE1 (-5.83 eV). The higher IP of alkoxy phenyl-containing polymers (HB-PAE3 and HB-PAE4) suggested their better stability when compared with more electron-rich carbazole-(HB-PAE1) and fluorene- (HB-PAE2) containing polymers. The HOMO energy level of L-PAE2 was found to -5.80 eV. The LUMO energy levels of polymers, calculated from optical band gap and the HOMO energy level were in the range -2.92 to -3.67 eV.

Electroluminescence Properties

To test the performances of the polymers, EL devices were fabricated using HB polymers HB-PAE1, HB-PAE2, HB-PAE4, and the linear polymer L-PAE2 as an emissive layer. The fabrication of the devices followed our earlier reported procedure.²² The concentration of the polymers in chlorobenzene was kept at 10 mg/mL. Typical EL spectra of the polymers were shown in Figure 8. The EL maxima of HB-PAE1, HB-PAE2, HB-PAE4, and L-PAE2 devices at 10 V are centered at 506, 535, 558, and 540 nm with Commission Internationale De L'Eclairage (CIE) coordinates at (0.21, 0.46), (0.35, 0.52), (0.47, 0.50), and (0.41, 0.55), respectively (Table 3). The EL of all polymers is red shifted with respect to the solid state PL. Similar red shift has been observed in other PAE systems, which is probably because of increased radiative decay from the longer conjugated segments during EL.^{1a}

Figure 9 shows the voltage–luminance characteristics (inset) of devices along with current density as a function of voltage. These data show that the turn-on voltages were 7.5, 10, 10, and 8.2 V for the HB-PAE1, HB-PAE2, HB-PAE4, and L-PAE2 devices, respectively. The low turn-on voltage of L-PAE2 device when compared with its HB analogs could be because of the better conjugation of rigid polymeric structure. A brightness of 490, 349, and 316 cd/m² could be achieved at a bias of 13, 15, and 15 V for HB-PAE1, HB-PAE2, and HB-PAE4 devices, respectively. Where as a brightness of 300 cd/m² could be achieved for L-PAE2 device at a

TABLE 3 Electroluminescent Properties of the Devices

Emitting Layer ^a	Turn-On Voltage (V) ^b	L _{max} (cd/m²) ^c	LE _{max} (cd/A) ^d	Emission (λ _{em} , nm)	CIE Coordinates (<i>x, y</i>) ^e
HB-PAE1	7.5	490	0.14	506	(0.21, 0.46)
HB-PAE2	10	349	0.08	535, 558	(0.35, 0.52)
HB-PAE4	10	316	0.11	558	(0.47, 0.50)
L-PAE2	8.2	300	0.075	540, 570	(0.41, 0.55)

^a Device configuration: ITO/PEDOT:PSS/emitting polymer/LiF/AI.

^b Turn-on voltage at 2 cd/m².

^c Maximum luminance.

^d Maximum current efficiency. ^e The 1993 CIE coordinates at 10 V.



FIGURE 9 Voltage-current density and voltage-luminance (inset) characteristics of the studied devices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bias of 14 V. The poor device performance of L-PAE2 could be because of the strong intermolecular interactions and aggregate formation of the linear polymers thereby quenching the fluorescence. Figure 10 shows the intensity of the emitted light as a function of wavelength and applied voltage for the HB-PAE1 device. As the driving voltage increases, the EL peak position and the CIE coordinates of the device were not found changed significantly. The EL emission stayed at 506 nm with the CIE color coordinates at (0.21, 0.46). As shown in Figures 11 and 12, a maximum current efficiency of 0.14 cd/A and power efficiency of 0.041 lm/W for the device ITO/PEDOT:PSS/HB-PAE1/LiF/Al was realized.

CONCLUSIONS

In summary, we successfully synthesized a series of PAEs with HB architecture. These polymers with TPA as core were found to be soluble in common organic solvents and show excellent film-forming properties. The polymers were found



FIGURE 10 EL spectra of HB-PAE1 at different applied voltages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 11 Current efficiency–current density characteristics of the studied devices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 12 Power efficiency–current density characteristics of the studied devices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to be highly fluorescent in nature and possess good thermal stability when compared with linear analogs. Double layer LEDs were fabricated using four of the synthesized polymers. The EL maxima of the polymers were in the range 506–558 nm. A maximum brightness upto 490 cd/m² could be achieved at a bias of 13 V for the ITO/PEDOT:PSS/HB-PAE1/LiF/Al device with CIE color chromaticity of (0.21, 0.46).

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