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Star-like fluorene based polyamines: non-conjugated building blocks for light-harvesting materials

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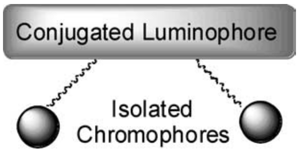
Abstract—We report herein a series of novel tetramines (**2**–**6**) built using the fluorene core. The design features a diamine conjugated by a fluorene core and two non-conjugated triarylamines dangling through the bridge methine moiety. These polyamines are amorphous in nature and display moderate emission properties that are either dependent on the nature of the arylamine segments or reminescent of the fluorene backbone. The phenyl, naphthyl, fluorenyl and carbazolyl amine based materials are blue emissive while the pyrenylamine based compound emits yellow-green color. We demonstrate a possibility of using blue-emitting fluorene derivatives (**2** and **4**) blended with poly(*N*-vinylcarbazole) (PVK) to fabricate organic light emitting diodes (OLEDs). Emissions in the EL devices purely originated from the fluorene derivatives alone (blue) are contaminated with those of complex species (electromer/electroplex) formed by intermolecular interactions.

1. Introduction

Triarylamines incorporating rigid and photoactive polyaromatics have recently attracted much attention in various research fields as advanced materials for electronic, photonic, and magnetic applications.[1] In particular, their use as hole transporting layers in organic light emitting diodes (LEDs) triggered the need of synthesizing thermally stable amorphous triarylamines with tunable luminescent characteristics.[2] We have earlier reported carbazole-,[2c–f] pyrene-,[3] and hexathienylbenzene-based[4] polyamines and they have been proved to be efficient hole transporting and/or emitting materials.

9,9-Dialkyl fluorene moieties have been used widely as building blocks in polymers and small molecules for photonic applications.[5] Incorporation of functional groups at 9 methine position and subsequent conversion into functional materials is rather rare. Fluorene containing crown ethers have been obtained exploiting the substitution at 9-position.[6] This also offers opportunity to design conjugated luminophores with non-conjugated functional units (shown as the following chart).



Such a site isolation technique has been recently demonstrated to be useful in obtaining advanced materials with both hole and electron-transporting capabilities besides emissive nature.[7] Also, suitably designed molecules could be useful systems for energy transfer studies.[8] It is interesting to note that a single blue-emitting phosphor[8] dopant in combination with its excimer emission can generate white light efficiently.

In this work, we report the synthesis and characterization of tetramines containing fluorene core. The four amines are positioned in such a way that two of them are interacting through the fluorene bridge while the remaining two triarylamines are dangling. We have fabricated devices containing PVK blended with these amines as host for carbazole based dopant emitter, 9-ethyl-*N*,*N*′-diphenyl-*N*,*N*′-dipyren-1-yl-9*H*-carbazole-3,6-diamine (carb9). The devices exhibited a mixed profile EL with a blue emission originating from the fluorene amine and a red electroplex (or electromer) emission. We also unravel that by varying the concentration of the fluorene amine, the ratio of the red electroplex (or electromer) emission to the blue emission

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Keywords: Excimer; Emission; Triarylamines.

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from the fluorene amine can be tuned. This allows us a possibility to demonstrate a white light emitting diodes.

2. Experimental

2.1. Materials

Unless otherwise specified all the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Toluene was distilled from sodium and benzophenone under nitrogen atmosphere. All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh) using hexane, dichloromethane mixtures.

The synthesis and characterization of 9-ethyl-*N*,*N*′-diphenyl-*N*,*N*′-dipyren-1-yl-9*H*-carbazole-3,6-diamine (carb9) has been published before.[9] The synthetic procedures of tris(8-quinolinolato)-aluminum(III) (Alq_3) as an electron-transporting layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole-blocking layer were reported in the literature.[11]

2.1.1. 2,7-Dibromo-9,9-bis-(4-bromo-benzyl)-9*H*-fluorene (1). A two-necked round bottom flask was charged with 2,7-dibromofluorene (3.24 g, 10 mmol), potassium *tert*-butoxide (3.36 g, 30 mmol) and dimethylsulfoxide (70 mL). After heating the contents to 50 °C, 4-bromobenzylbromide (6.0 g, 24 mmol) was added in small portions over 1 h. The reaction was continued for overnight at that temperature and quenched by pouring in ice. The solids formed were extracted with diethyl ether and purified by column chromatography (SiO_2, hexane–dichlormethane (8/2)) to yield 5.95 g (90%) of **1** as a colorless solid. ^1H NMR ($CDCl_3$): 3.26 (s, 4H, CH_2), 6.44–6.49 (m, 4H, ph), 7.02–7.07 (m, 4H, ph), 7.20 (d, $J=8.1$ Hz, 2H, flourene 4-CH), 7.35 (dd, $J=8.1$, 1.9 Hz, 2H, fluorene 3-CH), 7.52 (d, $J=1.9$ Hz, 2H, fluorene 2-CH). FAB MS (*m*/*z*): 662 (M^+). Anal. Calcd for $C_{27}H_{18}Br_4$: C, 48.98; H, 2.74. Found: C, 49.04; H, 2.67.

2.2. General amination procedure

A two-necked flask containing bromide (**1**), 4.4 equiv of diarylamine, $Pd(dba)_2$ (4 mol%), P(*t*-bu)$_3$ (4–8 mol%), sodium *tert*-butoxide (6 equiv) was added 20 mL toluene and heated at 80 °C for 12 h. After all the bromide was consumed, the reaction was quenched by the addition of ice water and extracted with diethyl ether. The organic extract was dried over anhydrous $MgSO_4$ and evaporated to dryness to yield the crude product. It was purified by column chromatography on silica gel using hexane and dichlomethane mixture as eluant. Typical yields range from 75 to 90%.

2.2.1. 9,9-Bis-(4-diphenylamino-benzyl)-*N*,*N*,*N*′,*N*′-tetraphenyl-9*H*-fluorene-2,7-diamine (2). Colorless solid. ^1H NMR (acetone-d_6): 3.34 (s, 4H, CH_2), 6.59–6.67 (m, 8H, ph), 6.85–6.88 (m, 8H), 6.91–6.99 (m, 10H), 7.03–7.06 (m, 8H), 7.15–7.24 (m, 16H), 7.41–7.45 (m, 4H). FAB MS (*m*/*z*): 1015 (M^+). Anal. Calcd for $C_{75}H_{58}N_4$: C, 88.72; H, 5.76; N, 5.52. Found: C, 88.65; H, 5.48; N, 5.49.

2.2.2. *N*,*N*′-Di-naphthalen-1-yl-9,9-bis-[4-(naphthalen-1-yl-phenyl-amino)-benzyl]-*N*,*N*′-diphenyl-9*H*-fluorene-2,7-diamine (3). Pale yellow solid. ^1H NMR (acetone-d_6): 3.81 (s, 4H, CH_2), 6.33–6.36 (m, 4H, ph), 6.47–6.50 (m, 4H, ph), 6.83–6.91 (m, 14H), 7.07–7.36 (m, 24H), 7.49 (q, $J=7.9$ Hz, 4H), 7.71–7.74 (m, 4H), 7.83 (t, $J=8.2$ Hz, 4H), 7.96 (dd, $J=7.9$, 3.1 Hz, 4H). FAB MS (*m*/*z*): 1216 (M^+). Anal. Calcd for $C_{91}H_{66}N_4$: C, 89.92; H, 5.47; N, 4.61. Found: C, 89.71; H, 5.59; N, 4.52.

2.2.3. *N*,*N*′-Bis-(9,9-diethyl-9*H*-fluoren-2-yl)-9,9-bis-{4-[(9,9-diethyl-9*H*-fluoren-2-yl)-phenyl-amino]-benzyl}-*N*,*N*′-diphenyl-9*H*-fluorene-2,7-diamine (4). Pale yellow solid. ^1H NMR (acetone-d_6): 0.22–0.31 (m, 24H, CH_3), 1.80–2.03 (m, 16H, CH_2), 3.38 (s, 4H, CH_2), 6.65 (d, $J=8.4$ Hz, 4H, ph), 6.77 (d, $J=8.4$ Hz, 4H, ph), 6.88–7.04 (m, 6H), 7.08–7.11 (m, 4H), 7.16–7.35 (m, 16H), 7.46 (d, $J=8.2$ Hz, 2H), 7.53–7.70 (m, 10H). FAB MS (*m*/*z*): 1592 (M^+). Anal. Calcd for $C_{119}H_{106}N_4$: C, 89.77; H, 6.71; N, 3.52. Found: C, 89.55; H, 6.73; N, 3.66.

2.2.4. *N*,*N*′-Diphenyl-9,9-bis-[4-(phenyl-pyren-1-yl-amino)-benzyl]-*N*,*N*′-di-pyren-1-yl-9*H*-fluorene-2,7-diamine (5). Yellow solid. ^1H NMR (acetone-d_6): 3.06 (s, 4H, CH_2), 6.36 (d, $J=8.4$ Hz, 4H, ph), 6.58 (d, $J=8.4$ Hz, 4H, ph), 6.73–6.76 (m, 2H), 6.83–6.88 (m, 8H), 6.95–7.00 (m, 8H), 7.19–7.25 (m, 4H), 7.34 (d, $J=1.9$ Hz, 2H), 7.41 (d, $J=8.2$ Hz, 2H), 7.47 (d, $J=7.5$ Hz, 2H), 7.59 (d, $J=9.5$ Hz, 2H), 7.65 (d, $J=8.1$ Hz, 3H), 7.68 (d, $J=8.2$ Hz, 2H), 7.88–8.08 (m, 14H), 8.14–8.20 (m, 8H), 8.27 (t, $J=8.4$ Hz, 4H). FAB MS (*m*/*z*): 1511.7 (M^+). Anal. Calcd for $C_{115}H_{74}N_4$: C, 91.36; H, 4.93; N, 3.71. Found: C, 91.23; H, 5.02; N, 3.54.

2.2.5. *N*,*N*′-Bis-(9-ethyl-9*H*-carbazol-3-yl)-9,9-bis-{4-[(9-ethyl-9*H*-carbazol-3-yl)-phenyl-amino]-benzyl}-*N*,*N*′-diphenyl-9*H*-fluorene-2,7-diamine (6). Pale yellow solid. ^1H NMR (acetone-d_6): 1.27 (t, $J=7.2$ Hz, 6H, CH_3), 1.38 (t, $J=7.2$ Hz, 6H, CH_3), 3.23 (s, 4H, CH_2), 4.28 (q, $J=7.2$ Hz, 4H, CH_2), 4.43 (q, $J=7.2$ Hz, 4H, CH_2), 6.57 (d, $J=8.4$ Hz, 4H, ph), 6.70–6.78 (m, 6H), 6.85–6.95 (m, 8H), 6.99 (d, $J=-7.6$ Hz, 4H), 7.03–7.19 (m, 14H), 7.23–7.32 (m, 6H), 7.35–7.44 (m, 8H), 7.48–7.55 (t, $J=9.5$ Hz, 4H), 7.76–7.79 (m, 4H), 7.92 (d, $J=1.9$ Hz, 2H), 7.98 (d, $J=7.7$ Hz, 2H). FAB MS (*m*/*z*): 1483.8 (M^+). Anal. Calcd for $C_{107}H_{86}N_8$: C, 86.61; H, 5.84; N, 7.55. Found: C, 86.56; H, 5.75; N, 7.41.

2.3. Preparation of devices

Glass slides precoated with indium tin oxide (ITO) with sheet resistances of ∼20 Ω/sq and with an effective individual device area of 3.14 mm^2 were used for fabrication of devices. The ITO glasses were routinely cleaned by ultrasonic treatment in detergent solutions, followed by through rinsing in acetone and then ethanol, and dried in oxygen plasma for 3 min before being loaded into the vacuum chamber. Since the molecular weight of the amines **2–6** are too large to be sublimed by thermal vacuum deposition for OLED devices, the amines **2–6** are blended with PVK to fabricate PLED devices and their photophysical properties are studied. The carb9 dopant and the amine derivatives **2–6** blended in PVK are dissolved in 1,2-dichloroethane with a concentration of 30 mg/mL and the spin coating rate was 3000 rpm for 40 s. The hole-blocking (BCP) and/or electron-transporting (Alq_3) layers were deposited thermally at a rate of 0.1–0.3 Å/s under a pressure of $\sim 2\times 10^{-5}$ Torr in an Ulvac Cryogenic deposition system. An alloy of magnesium and silver (ca. 10:1, 50 nm) was deposited as a cathode, which was then capped with 100 nm of silver.

2.4. Instrumentation

Dichloromethane for spectroscopic and voltammetric measurements were distilled from calcium hydride under nitrogen atmosphere. NMR spectra were recorded on Bruker 300 MHz spectrometer operating at 300.135 MHz. Electronic absorption spectra were obtained from a Cary 50 probe UV–visible spectrophotometer. Emission spectra were recorded on Perkin–Elmer spectrofluorometer. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin–Elmer DSC-7 at a heating rate of 10 °C/min under nitrogen atmosphere. Electrochemical measurements were performed in a BAS 100B electrochemical analyzer using a conventional three-electrode cell assembly comprising of glassy carbon working electrode, platinum auxiliary electrode and Ag/$AgNO_3$ reference electrode. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. Potentials were calibrated by using ferrocene as an internal standard. The photoluminescence (PL) and electroluminescence (EL) spectra were recorded on a Hitachi spectrofluorimeter. Diphenylamine, $Pd(dba)_2$ and 4-bromobenzylbromide were procured from commercial sources and used as received.

3. Results and discussion

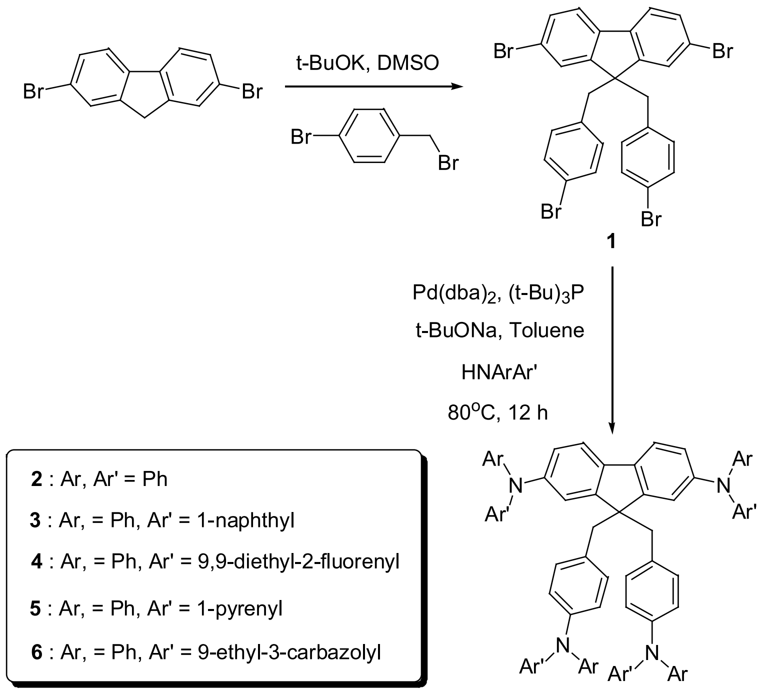
3.1. Synthesis

The synthetic procedure of fluorene based tetramines (**2–6**) is shown in Scheme 1. Tethering 4-bromobenzyl units on fluorene core is achieved by treating 2 equiv of 4-bromobenzyl bromide with 2,7-substituted fluorenes in the presence of potassium *t*-butoxide in dimethylsulfoxide. The resulting tetrabromide (**1**) undergoes facile cross coupling reactions with various diarylamines in the presence of $Pd(dba)_2$, (*tert*-Bu)$_3$P, and *tert*-BuONa to produce the target amines (**2–6**) in good yields.[10] The structures of the new compounds **1–6** have been confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis. The All amines are stable towards air in the solid state and soluble in commonly used organic solvents.

3.2. Thermal, photophysical and electrochemical properties

In order to ensure that these materials are useful in organic light emitting diode fabrications, the thermal, photophysical and electrochemical properties in dichloromethane solutions are surveyed. The pertinent data are listed in Table 1.

3.2.1. Thermal properties. All amine derivatives **2–6** form glasses and possess high glass transition temperatures (T_g). According to the rigidity of the substituents, the glass transition temperatures of the fluorene derivatives **2–6** (shown in Table 1) are in the following order: **5** (pyrenyl substituents) > **6** (carbazolyl substituents) > **3** (naphthyl substituents) > **4** (diethyl-fluorenyl substituents) > **2** (phenyl



Scheme 1. The synthetic route of fluorene based tetramines (**2–6**).

Table 1. Thermal, photophyscial and electrochemical data of the amines (**2**–**6**)

Compound	λ_{max} (ε_{max}) (nm) ($\times 10^{-3}$ M^{-1} cm^{-1})[a]	$\lambda_{PL,\ sol}$ (nm)	$\Phi_{PL,\ sol}$[b]	E_{ox} (ΔE_p) (mV)[c]	T_g (°C)[d]	HOMO/LUMO (eV)
2	366 (45.0)	398	0.40	392 (69)	101	5.00/1.81
3	364 (49.9)	432	0.06	375 (65)	132	4.98/1.88
4	337 (117.7)	408	0.72	343 (74)	125	4.95/1.93
5	378 (65.4)	464	0.05	362 (72)	185	4.98/2.28
6	375 (44.4)	426	0.15	237 (68)	156	4.85/1.71

[a] Only the lowest energy absorption peak and extinction coefficient are listed.

[b] Quantum yield (PL) was measured in dichloromethane with reference to coumarin-1 (0.99 in ethyl acetate).

[c] First oxidation potential values are quoted against Ag/AgNO^3 non-aqueous reference electrode.

[d] Glass transition temperature was measured at the heating rate of 10 °C/min.

substituents). Therefore, the glass transition temperature of **5** is substantially increased to the highest value (T_g = 185 °C) due to the highest rigidity of the pyrene units. We have reported the enhancement of T_g due to the presence of pyrene for carbazole derivatives earlier.[2c,3]

3.2.2. Photophysical properties. Absorption and PL emission spectra of the fluorene derivatives **2**–**6** are shown in Figure 1a and b. All the amines (**2**–**6**) display two prominent transitions in the absorption spectra. The red shifted absorption in each amine is attributed to the π–π* transition of the fluorene backbone end-capped with terminal amines. The higher energy absorption with larger optical density probably originates from the *n*–π* transition of the triarylamine segments. All the compounds emit in the blue region except **5**, which displays green color in photoluminescence (PL) and electroluminescence (EL) spectra (Fig. 1). The amines containing naphthalenyl and pyrenyl units (**3** and **5**) exhibit broad and structureless emissions with relatively large Stokes shifts and low quantum yields in PL. This is clearly indicative of excimer formation at the excited state.[12] This intramolecular excimer formation has been also realized earlier for certain non-conjugative molecules possessing multiple pyrene segments.[13] Moreover, careful examination of emission maxima and pattern reveals that the emission in tetramines (**2**–**6**) originates from the main fluorene backbones. Hence, due to the additional contribution from the star-branched diethyl-fluorenyl substituents in **4**, it possesses the highest quantum yield ($\Phi_{PL,\ sol}$ = 0.72) among all amine derivatives.

3.2.3. Electrochemical properties. Two reversible oxidations corresponding to one and three electrons, respectively, were located in the cyclic voltammograms of the amines **2**–**6**. The electron count is by analogy with the intensity of the redox wave of the internal standard ferrocene. In the amines **2**–**6**, the first one electron oxidation must stem from one of the diarylamine units attached directly to the fluorene cores. This suggestion is also in agreement with the oxidation potential values. Diphenylamino and 1-naphthyl phenylamino segments generally possess high oxidation potentials if they are connected to phenyl or related aromatics.[2,12] It is also interesting to note that the first oxidation potentials in these fluorene derivatives (**2**–**6**) are reminiscent of the electron richness of the capping diarylamine units and they are cathodically shifted in the following order: diphenylamine > 1-naphthylphenylamine > 1-pyrenylphenylamine > 9,9-diethyl-2-fluorenylphenylamine > 9-ethyl-3-carbazolylphenylamine.

3.3. Electro-optical properties

The EL devices were made by blending the newly synthesized amines with the polymer PVK in appropriate ratios. For a device structure of ITO/PVK:**X** (**X** = **2**) (100:50 by weight)/BCP (5 nm)/Alq_3 (15 nm)/MgAg (50 nm)/Ag (100 nm) the EL spectra displayed features due to the amine and a distinct band at ca. 600 nm. However, this red shifted profile is not present in the PL spectra for the blends (see for instance Fig. 2a). This strongly implies that the EL emission peak at ~600 nm is owing to the formation of electromers[14] from **2** or electroplexes[15] from the interface of **2** and PVK. We also observe that the addition of carb9 to the PVK:**2** blend, completely suppresses the intrinsic emission of **2**

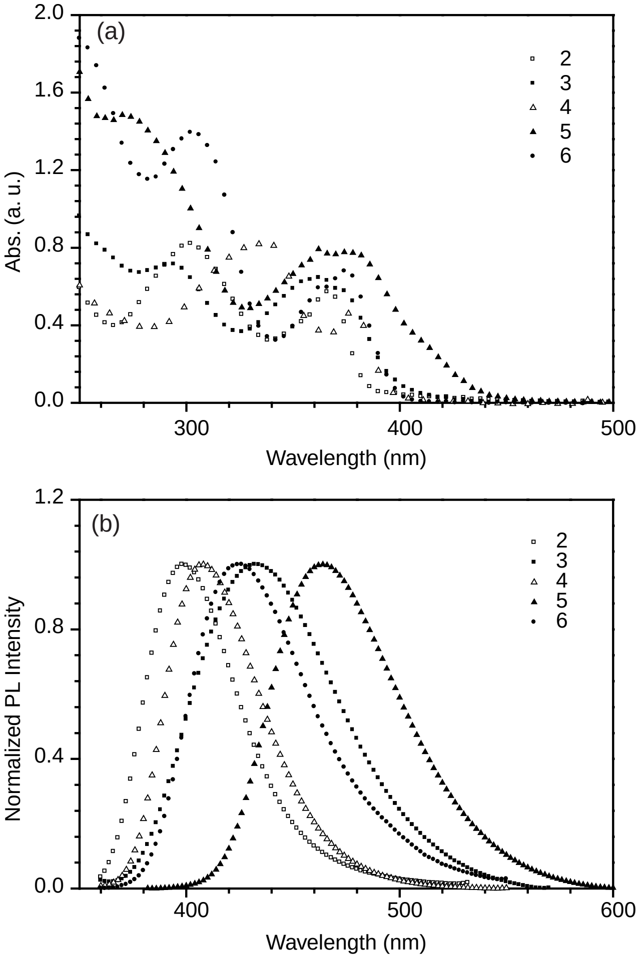


Figure 1. Absorption (a), PL emission (excitation at 350 nm) (b) spectra of **2**–**6** recorded in dichloromethane solutions.

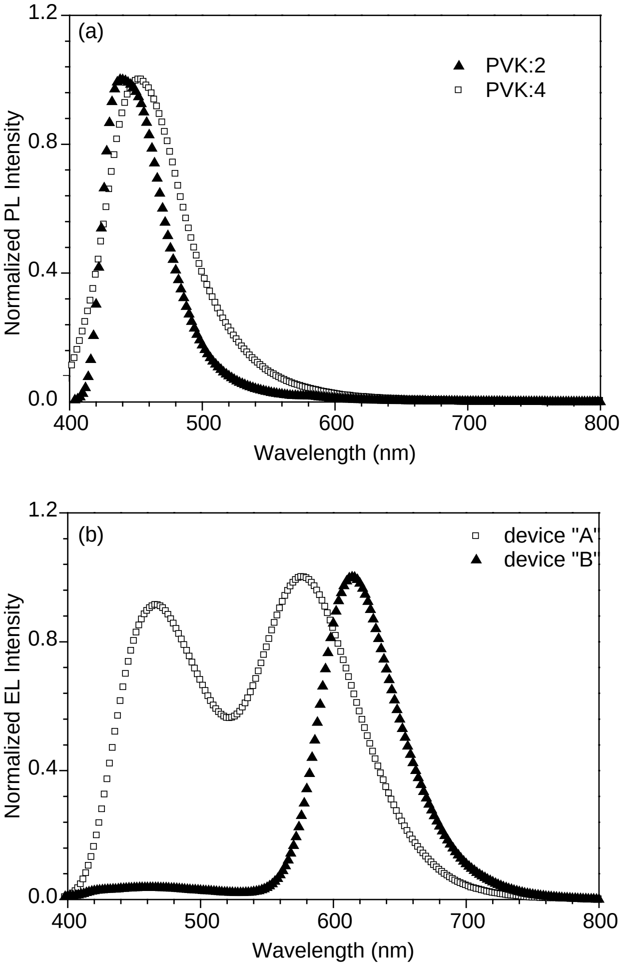


Figure 2. (a) PL spectra of PVK:**2** (or **4**) blend films and (b) EL spectra of the devices A (ITO/PVK:**2**:carb9 (100:200:20 by weight)/BCP (5 nm)/Alq_3 (15 nm)/MgAg (50 nm)/Ag (100 nm)) and B (ITO/PVK:**4**:carb9 (100:300:5 by weight)/BCP (10 nm)/Alq_3 (20 nm)/MgAg (50 nm)/Ag (100 nm)).

(ca. 420 nm). This is possibly due to the efficient energy transfer from **2** and/or PVK to carb9, which emits at ∼460 nm. So the EL spectra of the devices that contained the matrix composition PVK:**X** (**2** or **6**):carb9 exhibit features due to carb 9 and electroplex/electromer emission. Subsequently we have tested two devices with the following configurations: the device ‘A’ of ITO/PVK:**2**:carb9 (100:200:20 by weight)/BCP (5 nm)/Alq_3 (15 nm)/MgAg (50 nm)/Ag (100 nm) and the device ‘B’ of ITO/PVK:**4**:carb9 (100:300:5 by weight)/BCP (10 nm)/Alq_3 (20 nm)/MgAg (50 nm)/Ag (100 nm). In fact, these two example devices were taken from a series of engineering work done by altering the composition of blend. The EL spectra obtained from these devices are displayed in Figure 2b. From that it is clearly evident that by adjusting the composition of the PVK:**X**:carb9 blend it is possible to realize either the white or red emission. In general, lesser concentration of carb9 leads to red electroplex/electromer emission while higher dopant ratio enhances the emission contribution from carb9 thus leading to white emission. The optimum performance of these devices has a brightness reaching 17368 cd/m^2 (maximum external quantum efficiency: 1.84%, CIE coordinate = 0.33, 0.35) for white light emission and 3440 cd/m^2 for orange-red-light emission (maximum external quantum efficiency: 0.42%, CIE coordinate = 0.60, 0.29). Full details on the EL characteristics will be published elsewhere.

4. Conclusions

In conclusion, we have synthesized a series of star-like fluorene based polyamines possessing novel photophysical properties. This strategy may be extended further to obtain discrete macromolecules and polymers with insulated functional chromophores (site isolation) or multi-functional moieties. We observed that by altering the aromatic substituents on the amine functionality the emission wavelength and glass transition temperature of the compounds can be tuned. The EL devices fabricated using the blends of these amines with PVK were investigated. They exhibited intense electroplex/electromer emission and by doping carb9 in those blends we demonstrate an unique way of fabricating white light emitting devices with good performance characteristics.

Acknowledgements

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