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Synthesis and luminescence properties of poly(*p*-phenylenevinylene) derivatives carrying directly attached carbazole pendants

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New organic soluble poly(*p*-phenylenevinylene) (PPV) derivatives (polymers **1** and **2**) that carry hole-transporting carbazole pendants were synthesized and their photo- and electro-luminescence properties were studied. The first one is poly[2-(carbazol-9-yl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (polymer **1**) which has both carbazole and 2-ethylhexyloxy pendant groups. The other one is poly[2-(carbazol-9-yl)-1,4-phenylenevinylene] (polymer **2**) which has only the carbazole pendant group attached to the main chain phenylene ring. We fabricated single-layer EL devices using indium–tin oxide (ITO) coated glass anodes and aluminium cathodes and investigated their electrical characteristics. The EL device of polymer **2** emits green light ($\lambda_{max} = 490$ nm) with the EL efficiency being lower than that of PPV. But the EL device of polymer **1** emits bright yellow–green light ($\lambda_{max} = 530$ nm) and its external quantum efficiency was 550 times the efficiency of polymer **2** and 60 times that of a PPV EL device with the same configuration. Especially, the EL device with the configuration ITO coated glass/poly(3,4-ethylenedioxy-2,4-thienylene)/polymer **1**/Ca/Al showed a low turn-on electric field of 0.31 MV cm^{-1} and a high photometric efficiency of 4.4 cd A^{-1} with maximum luminance being 30 390 cd m^{-2} at an electric field of 1.50 MV cm^{-1}. Polymer **1** appears to perform better in EL than MEH-PPV.

Introduction

Electroluminescent devices based on organic polymeric materials have attracted a considerable amount of attention due to possible applications in large-area light-emitting displays.[1–9] It is understood that in light emitting diode (LED) devices electrons and holes are separately injected from an anode and a cathode, respectively, under a bias voltage into the light emitting polymer layer, where the injected negative and positive carriers form excitons.[1,10] The excitons can disappear *via* various mechanisms; one of them is luminescent decay or radiative decay. In order to improve the efficiency of LEDs, there have been many attempts to balance the injection of carriers from electrodes and also their mobility in the polymer layer. Tang and Van Slyke[11] demonstrated that the use of a hole-transporting layer (HTL) for facile hole injection from the anode into the emission layer significantly lowers the drive voltage and improves the device performance. Poly(vinylcarbazole), a polymer which has the carbazole moieties as pendants, is known to be an excellent hole-transporting material[12] and low molecular weight carbazole derivatives and carbazole containing polymers have also recently been used as hole-transporting materials.[13–18]

However most studies of carbazole polymers have been limited to the use of the material as a hole-transporting layer or as host polymer for doping with organic dyes. Recently, some researchers reported luminescence properties of polymers that have carbazole moieties in the main chain or as side pendants.[19–22]

We have synthesized two polymers carrying carbazole moieties attached directly to the phenylene rings in the backbone of the PPV structure. The first one is poly[2-(carbazol-9-yl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (polymer **1**, Scheme 1) which has both carbazole and 2-ethylhexyloxy pendant groups. The other is poly[2-(carbazol-9-yl)-1,4-phenylenevinylene] (polymer **2**, Scheme 2) which has only the carbazole pendant group attached to the main chain. We previously reported briefly the luminescence properties of polymer **2**.[8] The LED device of polymer **2** showed a rather poor electroluminescence efficiency even when compared with PPV. Attachment of a good hole-transporter may imbalance the carrier mobilities even further. PPV itself is known to be a much better hole-transporter than electron-transporter.[23] This factor could decrease the EL efficiency of the device of polymer **2**. Another problem noted is that it possesses a high HOMO (highest occupied molecular orbital) energy level (6.1 eV), which requires a high drive voltage for hole injection from the ITO anode to the emitting polymer layer. Moreover, the solubility of polymer **2** was found unsatisfactory to form films of good quality.

Polymer **1** (Scheme 1) carries additional electron-donating alkoxy groups attached to the phenylene ring. The bulky alkoxy group could reduce the possibility of formation of interchain excitons[24,25] by increasing the interchain distance that is claimed to cause a lower EL efficiency[26–28] and also improves polymer solubility giving rise to a higher film quality. In addition, we expected the electron donating alkoxy group to reduce the HOMO energy level and lower the drive voltage due to facilitated hole injection from the cathode.

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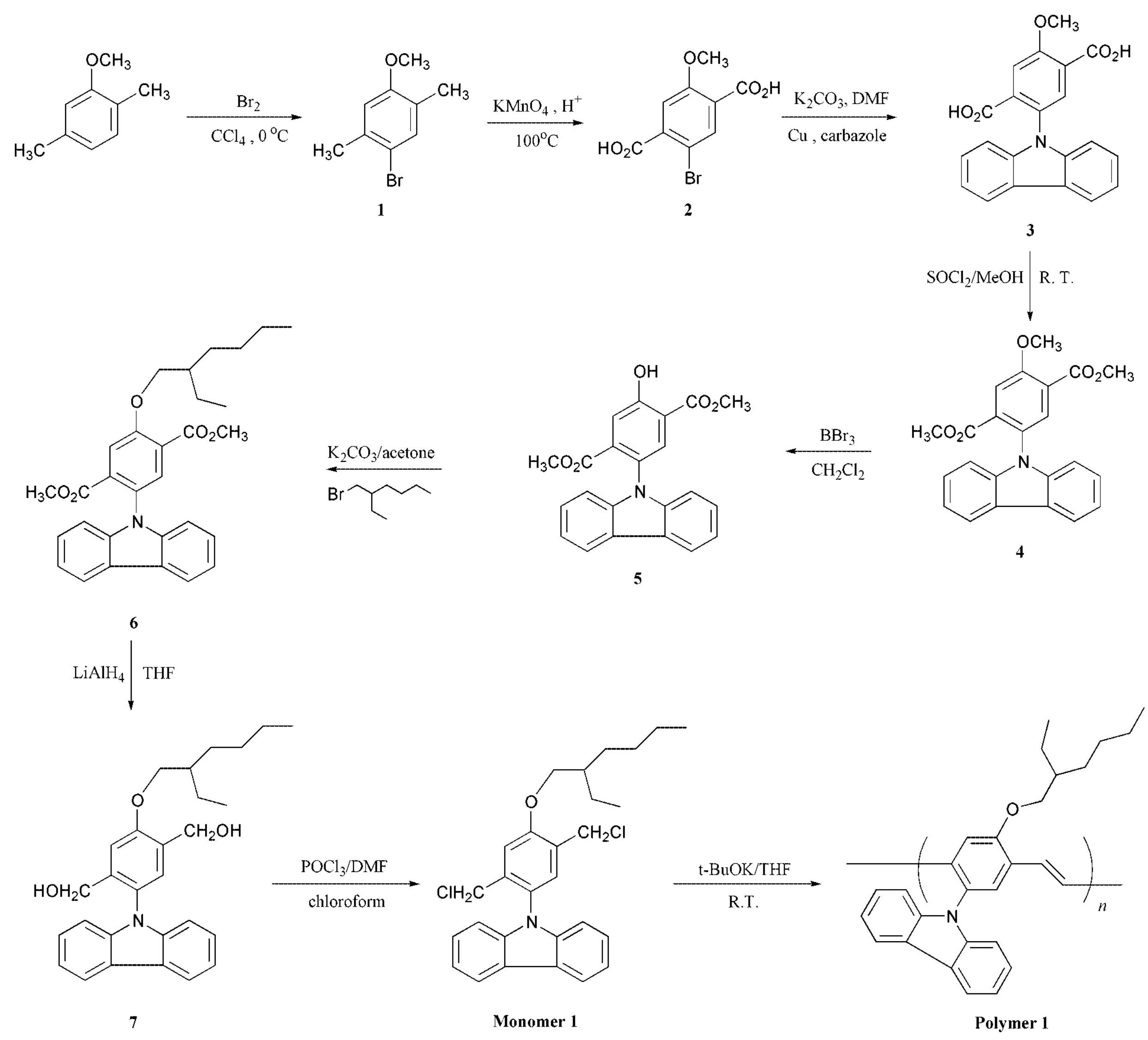


Scheme 1 Synthetic route to monomer **1** and polymer **1**.

Experimental

A. Synthesis

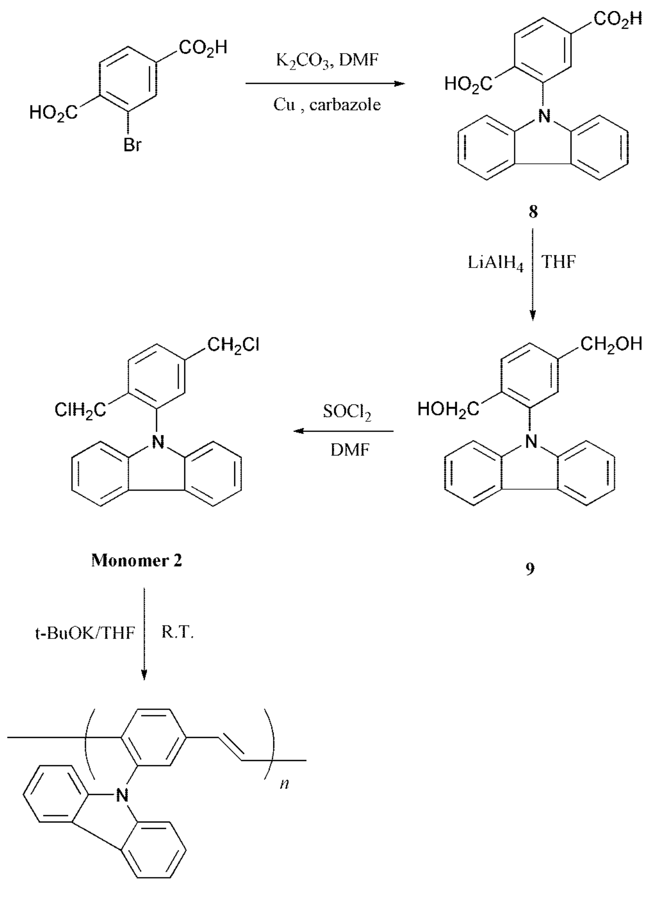
Chemicals and instruments. All the chemicals were obtained commercially from Aldrich or Junsei. They were of analytical or higher grade and used without further purification. Solvents to be used under anhydrous conditions were dried by standard methods. Infrared spectra were recorded on an FT-IR Bomem Michaelson instrument. ^{1}H-NMR spectra were recorded on a Varian Gemini 300 spectrometer.

Synthesis of monomers and polymers. Synthesis of monomers and polymers are outlined in Schemes 1 and 2. Synthetic details are described below following the synthetic routes shown in the schemes.

4-Bromo-2,5-dimethylanisole, 1. To a solution of 2,5-dimethylanisole (60.3 g; 0.443 mol) dissolved in 600 mL of chloroform was added dropwise at 0 °C a solution of bromine (70.2 g; 0.441 mol) in carbon tetrachloride (200 mL). After 7 h of stirring at 0 °C, saturated aqueous NaOH solution (300 mL) was added to the reaction mixture and the organic phase was separated and washed with distilled water. After the solvent was removed by evaporation, the impure product was chromatographed on a silica gel column using methylene chloride as an eluent to afford the title compound as an oil (83.1 g; 87.2% yield). Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15. Found: C, 50.28; H, 5.19%. ^{1}H-NMR (acetone-d_6; δ/ppm): 2.1 (s, 3H, -CH_3), 2.3 (s, 3H, -CH_3), 3.8 (s, 3H, CH_3O-), 6.9 (s, 1H, Ar-*H*), 7.2 (s, 1H, Ar-*H*). IR (KBr, cm^{-1}): 3051 (aromatic C–H stretch), 2957 (aliphatic C–H stretch), 1602, 1480 (Ar C=C stretch), 1205, 1101 (C–O stretch).

2-Bromo-5-methoxyterephthalic acid, 2. A mixture of **1** (40.6 g; 0.189 mol) and $KMnO_4$ (300 g; 1.90 mol) was refluxed for 24 h in water (2.5 L) with vigorous stirring. The hot reaction mixture was filtered through a suction filter and the cake of hydrated manganese dioxide on the filter was washed with water. The combined filtrate was acidified cautiously by adding 35% hydrochloric acid with continual agitation. The white precipitate was collected on a filter and washed with cold water (33.7 g; 64.8% yield), mp 275 °C. Anal. Calcd for $C_9H_7BrO_5$: C, 39.30; H, 2.57. Found: C, 39.27; H, 2.56%. ^{1}H-NMR (acetone-d_6; δ/ppm): 3.0 (s, 2H, -CO*OH*), 4.0 (s, 3H, CH_3O-), 7.5 (s, 1H, Ar-*H*), 8.0 (s, 1H, Ar-*H*). IR (KBr, cm^{-1}): 3350–2400 (O–H stretch of acid), 1700 (C=O stretch), 1600, 1475 (Ar C=C stretch), 1248, 1109 (C–O stretch).

2-(Carbazol-9-yl)-5-methoxyterephthalic acid, 3. A mixture of **2** (10.0 g; 0.0364 mol), carbazole (12.0 g; 0.0718 mol), K_2CO_3 (12.4 g; 0.0897 mol) and copper powder (0.301 g) in *N*,*N*-dimethylformamide (300 mL) was refluxed for 48 h.[29] The reaction mixture was cooled and the solvent was evaporated. Crude product was extracted with water followed by washing



Scheme 2 Synthetic route to monomer **2** and polymer **2**.

with ether. The aqueous phase was acidified cautiously by adding 35% hydrochloric acid with continual agitation. The yellow precipitate was collected on a filter and recrystallized from chloroform (11.0 g; 83.6% yield), mp 298 °C. Anal. Calcd for $C_{21}H_{15}NO_5$: C, 69.80; H, 4.18; N, 3.88. Found: C, 69.86; H, 4.14; N, 3.83%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 4.1 (s, 3H, *CH$_3$*O-), 7.1 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.8 (s, 1H, Ar-*H*), 7.9 (s, 1H, Ar-*H*), 8.1 (d, 2H, Ar-*H*), 11.4 (s, 2H, CO*OH*). IR (KBr, cm^{-1}): 3400–2400 (O–H stretch of acid), 1700 (C=O stretch), 1598, 1460 (Ar C=C stretch), 1310 (C–N stretch), 1234, 1172 (C–O stretch).

Dimethyl 2-(carbazol-9-yl)-5-methoxyterephthalate, 4. Compound **3** (4.40 g; 0.0122 mol) was dissolved in 300 mL of methanol. To this solution was slowly added purified thionyl chloride[30] (17.5 mL) with stirring over a period of 1 h. The mixture was stirred for 12 h at room temperature. Then the reaction mixture was poured into a large excess of distilled water. To the slurry was added a 10% aqueous solution of $NaHCO_3$ until the mixture became neutral. The precipitate formed was collected on a filter and washed with distilled water. The product was recrystallized from methanol (4.39 g; 92.4% yield), mp 145 °C. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.96; H, 4.91; N, 3.58%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 3.2 (s, 3H, -CO$_2$*CH$_3$*), 3.8 (s, 3H, -CO$_2$*CH$_3$*), 4.0 (s, 3H, *CH$_3$*O-), 7.1 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.7 (s, 1H, Ar-*H*), 7.9 (s, 1H, Ar-*H*), 8.2 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3050 (aromatic C–H stretch), 2948 (aliphatic C–H stretch), 1727 (C=O stretch), 1600, 1470 (Ar C=C stretch), 1300 (C–N stretch), 1223, 1106 (C–O stretch).

Dimethyl 2-(carbazol-9-yl)-5-hydroxyterephthalate, 5. Compound **4** was dissolved in 300 mL of CH_2Cl_2. To this solution was introduced dropwise at 0 °C 1 M BBr_3 (17.8 mL; 0.018 mol).[31] The mixture was stirred for 4 h at 0 °C. The mixture was then poured into a large excess of distilled water. The organic phase was washed with distilled water. The organic layer was separated and the solvent was evaporated. Chromatography (silica gel, CH_2Cl_2 eluent) of the residue afforded the title compound as a yellow solid (2.9 g; 87% yield), mp 80 °C. Anal. Calcd for $C_{22}H_{17}NO_5$: C, 70.39; H, 4.56; N, 3.73. Found: C, 70.31; H, 4.51; N, 3.71%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 3.2 (s, 3H, -CO$_2$*CH$_3$*), 3.9 (s, 3H, -CO$_2$*CH$_3$*), 7.1 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.6 (s, 1H, Ar-*H*), 7.9 (s, 1H, Ar-*H*), 8.2 (d, 2H, Ar-*H*), 10.7 (s, 1H, Ar-*OH*). IR (KBr, cm^{-1}): 3210 (O–H stretch), 3071 (aromatic C–H stretch), 2957 (aliphatic C–H stretch), 1727 (C=O stretch), 1595, 1452 (Ar C=C stretch), 1327 (C–N stretch), 1205, 1101 (C–O stretch).

Dimethyl 2-(carbazol-9-yl)-5-(2-ethylhexyloxy)terephthalate, 6. A mixture of **5** (2.91 g; 0.775×10^{-2} mol), K_2CO_3 (2.20 g; 0.0159 mol) and tetrabutylammonium bromide (0.1 g) in acetone (300 mL) was refluxed for 24 h. The solid residue was removed by filtration. Acetone in the filtrate was evaporated. The product was recrystallized from methanol (3.60 g; 95.2% yield), mp 138 °C. Anal. Calcd for $C_{30}H_{33}NO_5$: C, 73.90; H, 6.82; N, 2.87. Found: C, 73.85; H, 6.74; N, 2.81%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 0.9–1.0 (m, 6H, -OCH$_2$CH-(CH$_2$*CH$_3$*)CH$_2$CH$_2$CH$_2$*CH$_3$*), 1.4 (m, 4H, -CH$_2$*CH$_2$CH$_2$*CH$_3$), 1.5–1.6 (m, 4H, -OCH$_2$CH(*CH$_2$*CH$_3$)*CH$_2$*CH$_2$CH$_2$CH$_3$), 1.8 (m, 1H, -OCH$_2$*CH*-), 3.2 (s, 3H, -CO$_2$*CH$_3$*), 3.8 (s, 3H, -CO$_2$*CH$_3$*), 4.2 (d, 2H, -O*CH$_2$*CH-), 7.1 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.7 (s, 1H, Ar-*H*), 7.8 (s, 1H, Ar-*H*), 8.1 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3061 (aromatic C–H stretch), 2948 (aliphatic C–H stretch), 1729 (C=O stretch), 1600, 1475 (Ar C=C stretch), 1310 (C–N stretch), 1223, 1101 (C–O stretch).

1,4-Bis(hydroxymethyl)-5-(2-ethylhexyloxy)-2-(carbazol-9-yl)-benzene, 7.[32] To a stirred mixture of $LiAlH_4$ (0.94 g; 0.25×10^{-2} mol) in dry tetrahydrofuran (THF)[30] (300 mL) was added dropwise a solution of **6** (4.0 g; 0.82×10^{-2} mol) in dry THF[30] (150 mL), and the mixture was refluxed for 4 h. The reaction mixture was cooled and 0.9 mL of water, 0.9 mL of 15% NaOH and 2.7 mL of water were added successively. Then, the solid residue was removed by filtration and the filtrate was dried over anhydrous $MgSO_4$, and the solvent was evaporated to obtain the product. The product thus obtained was utilized in the next step without further purification (3.4 g; 97% yield), mp 128 °C. Anal. Calcd for $C_{28}H_{33}NO_3$: C, 77.93; H, 7.71; N, 3.25. Found: C, 77.92; H, 7.70; N, 3.24%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 0.9–1.0 (m, 6H, -OCH$_2$CH(CH$_2$*CH$_3$*)-CH$_2$CH$_2$CH$_2$*CH$_3$*), 1.4 (m, 4H, -CH$_2$*CH$_2$CH$_2$*CH$_3$), 1.5–1.6 (m, 4H, -OCH$_2$CH(*CH$_2$*CH$_3$)*CH$_2$*CH$_2$CH$_2$CH$_3$), 1.8 (m, 1H, -OCH$_2$*CH*-), 4.0 (d, 2H, -*CH$_2$*OH), 4.1 (t, 1H, -CH$_2$*OH*), 4.2 (d, 2H, -*CH$_2$*OH), 4.2 (t, 1H, -CH$_2$*OH*), 4.7 (d, 2H, -O*CH$_2$*CH-), 7.0 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.4 (s, 1H, Ar-*H*), 7.4 (s, 1H, Ar-*H*), 8.2 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3367 (O–H stretch), 3054 (aromatic C–H stretch), 2913 (aliphatic C–H stretch), 1598, 1460 (Ar C=C stretch), 1310 (C–N stretch), 1223, 1014 (C–O stretch).

1,4-Bis(chloromethyl)-5-(2-ethylhexyloxy)-2-(carbazol-9-yl)-benzene, monomer 1. To a solution of **7** (1.2 g; 0.29×10^{-2} mol) in dry chloroform[30] (250 mL) was added with stirring a solution of dimethylformamide (0.15 mL; 0.19×10^{-2} mol) and phosphoryl chloride[30] (0.18 mL; 0.19×10^{-2} mol) in dry chloroform[30] (150 mL) and stirring was continued for 24 h at room temperature. The solvent was evaporated. The residue was stirred with cold water and ether. The ethereal layer was separated and was dried over calcium chloride. Ether was removed by evaporation from the solution leaving behind the crude product. Chromatography (silica gel, hexane) of the residue afforded the title compound as an oil (1.0 g; 76% yield). Anal. Calcd for $C_{28}H_{31}Cl_2NO$: C, 71.79; H, 6.67; N, 2.29. Found: C, 71.78; H, 6.65; N, 2.27%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 0.8–1.0 (m, 6H, -$OCH_2CH(CH_2\mathit{CH_3})CH_2CH_2CH_2\mathit{CH_3}$), 1.4 (m, 4H, -$CH_2\mathit{CH_2CH_2}CH_3$), 1.5–1.7 (m, 4H, -$OCH_2CH$-($\mathit{CH_2}CH_3)\mathit{CH_2}CH_2CH_2CH_3$), 1.8 (m, 1H, -$OCH_2\mathit{CH}$-), 4.2 (d, 2H, -$O\mathit{CH_2}CH$-), 4.4 (s, 2H, $\mathit{CH_2}Cl$), 4.8 (s, 2H, -$\mathit{CH_2}Cl$), 7.0 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.4 (s, 1H, Ar-*H*), 7.5 (s, 1H, Ar-*H*), 8.2 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3050 (aromatic C–H stretch), 2934 (aliphatic C–H stretch), 1596, 1452 (Ar C=C stretch), 1325 (C–N stretch), 1234, 1185 (C–O stretch), 646 (C–Cl stretch).

Poly[2-(carbazol-9-yl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], polymer 1. To a solution of monomer **1** (1.0 g; 0.21 × 10^{-2} mol) in purified THF[30] (70 mL) was added dropwise at 0 °C a solution of 1 M potassium *tert*-butoxide in THF (12 mL) *via* a syringe over a period of 10 minutes.[33] The mixture was stirred for 6 h at room temperature. The colorless solution turned orange and became viscous. After reacting for an additional 18 h at room temperature, the polymer formed was precipitated by slow addition of methanol to the reaction mixture. Subsequent dissolving in THF and precipitating in methanol three times yielded an orange colored polymer. The product was subjected to Soxhlet extraction for 24 h using methanol (3.5 g; 44% yield). The molecular weight of this polymer determined by GPC measurement with polystyrene as the calibration standard was $\bar{M}_w = 72\,000$ and $\bar{M}_w = 49\,800$ with a polydispersity index (PDI) of 1.4.

Anal. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54. Found: C, 85.50; H, 6.95; N, 3.43%. ^{1}H-NMR ($CDCl_3$; δ/ppm): 0.83–1.92 (m, 15H, -$CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 3.98 (d, 2H, -$O\mathit{CH_2}CH$-), 6.58 (d, 2H, -CH=CH-), 6.77–7.26 (m, 8H, Ar-*H*), 7.89 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3058 (aromatic C–H stretch), 2925 (aliphatic C–H stretch), 1727 (C=O stretch), 1598, 1476 (Ar C=C stretch), 1311 (C–N stretch), 1227, 1194 (C–O stretch), 969 (*trans* = CH out-of-plane bending).

2-(Carbazol-9-yl)terephthalic acid, 8. A mixture of 2-bromoterephthalic acid (5.0 g, 0.020 mol), carbazole (6.8 g; 0.041 mol), K_2CO_3 (1.4 g; 0.010 mol) and copper powder (0.15 g) was mixed in DMF (250 mL) and the mixture was refluxed for 48 h.[29] The reaction mixture was worked up the same way as in the preparation of compound **3**. The crude yellow precipitate was recrystallized from a mixture of water and methanol (1 : 2 by volume) (5.0 g; 75% yield), mp 290 °C. Anal. Calcd for $C_{20}H_{13}NO_4$: C, 72.50; H, 3.95; N, 4.23. Found: C, 72.31; H, 3.92; N, 4.21%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 7.1 (d, 2H, Ar-*H*), 7.2 (t, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 8.1 (d, 2H, Ar-*H*), 8.2 (s, 1H, Ar-*H*), 8.2 (d, 1H, Ar-*H*), 8.2 (d, 1H, Ar-*H*), 11.8 (s, 2H, CO*OH*). IR (KBr, cm^{-1}): 3600–2300 (O–H stretch of acid), 1700 (C=O stretch), 1591, 1454(Ar C=C stretch), 1310 (C–N stretch).

2-(Carbazol-9-yl)-1,4-bis(hydroxymethyl)benzene, 9. To a stirred mixture of $LiAlH_4$ (1.8 g; 0.048 mol) in dry THF[30] (200 mL) was added dropwise a solution of **8** (3.2 g; 0.97 × 10^{-2} mol) in dry THF[30] (200 mL) and the mixture was refluxed for 2 h. The reaction mixture was treated as the same way as in the preparation of compound **7**. Chromatography (silica gel, hexane–ethyl acetate = 1 : 1 by volume) of the crude residue afforded the title compound as an oil (1.6 g, 55% yield). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 78.94; H, 5.54; N, 4.59%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 4.2 (t, 1H, -$CH_2\mathit{OH}$), 4.3 (d, 2H, -$\mathit{CH_2}OH$), 4.5 (t, 1H, -$CH_2\mathit{OH}$), 4.8 (d, 2H, -$\mathit{CH_2}OH$), 7.1 (d, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.4 (t, 2H, Ar-*H*), 7.4 (s, 1H, Ar-*H*), 7.6 (d, 1H, Ar-*H*), 7.9 (d, 1H, Ar-*H*), 8.3 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3342 (O–H stretch), 3051 (aromatic C–H stretch), 2914 (aliphatic C–H stretch), 1590, 1448 (Ar C=C stretch), 1312 (C–N stretch).

2-(Carbazol-9-yl)-1,4-bis(chloromethyl)benzene, monomer 2. To a solution of **9** (2.0 g; 0.65 × 10^{-2} mol) in DMF (150 mL) was added dropwise at 15 °C purified $SOCl_2$[30] (3.1 g; 0.026 mol). After 2 h of stirring at 10–15 °C, DMF and excess $SOCl_2$ were distilled out *via* vacuum distillation. Chromatography (silica gel, hexane–CH_2Cl_2 = 1 : 1 by volume) of the residue afforded the title compound as an oil (2.1 g; 95% yield). Anal. Calcd for $C_{20}H_{15}Cl_2N$: C, 70.60; H, 4.44; N, 4.12. Found: C, 70.11; H, 4.34; N, 4.05%. ^{1}H-NMR (acetone-d$_6$; δ/ppm): 4.4 (s, 2H, -$\mathit{CH_2}Cl$), 4.9 (s, 2H, -$\mathit{CH_2}Cl$), 7.1 (d, 2H, Ar-*H*), 7.3 (t, 2H, Ar-*H*), 7.4 (t, 2H, Ar-*H*), 7.6 (s, 1H, Ar-*H*), 7.8 (d, 1H, Ar-*H*), 7.9 (d, 1H, Ar-*H*), 8.3 (d, 2H, Ar-*H*). IR (KBr, cm^{-1}): 3050 (aromatic C–H stretch), 2950 (aliphatic C–H stretch), 1590, 1447 (Ar C=C stretch), 1310 (C–N stretch), 680 (C–Cl stretch).

Poly[2-(carbazol-9-yl)-1,4-phenylenevinylene], polymer 2. The polymerization method for polymer **2** was the same as polymer **1**. Anal. Calcd for $C_{20}H_{13}N$: C, 89.86; H, 4.90; N, 5.24. Found: 89.87; H, 4.89; N, 5.23%. IR (KBr, cm^{-1}): 3050 (aromatic C–H stretch), 2945 (aliphatic C–H stretch), 1598, 1476 (Ar C=C stretch), 1311 (C–N stretch).

B. Device fabrication and characterization

ITO/polymer 1 or 2/Al and ITO/polymer 1 or 2/Li : Al devices. Indium–tin oxide (ITO) coated glass slides with a sheet resistance of 25 Ω cm^{-2} were patterned by the vapor of a mixed solution of HNO_3 and HCl in a volume ratio of 3 : 1. The patterned ITO-coated glass slides were cleaned by sequential ultrasonication in acetone, methanol and propan-2-ol for 20 minutes, then dried in a stream of nitrogen.

The solution (1 wt%) of polymer **1** or **2** in purified 1,1,2,2-tetrachloroethane[30] was spin-coated on a 1.2 cm × 1.2 cm ITO-coated glass in argon atmosphere using a Laurell (USA) spin-coater. The spin-coated polymer layer was annealed under 10^{-3} Torr at 150 °C for 2 hours to remove the residual 1,1,2,2–tetrachloroethane solvent and to ensure complete dehydrochlorination.

The Al or Li : Al alloy (Li 0.2 wt%) electrode 1500 Å thick was vapor deposited using a LEYBOLD L560 (Germany) apparatus at a deposition rate of 5 Å s^{-1} onto the polymer layer at a pressure of 1 × 10^{-6} Torr. Deposition of the cathode electrode was conducted at the Korea Basic Science Institute – Seoul Branch, Korea. The active area of the device was 4.9 mm^2. The thickness of polymer was determined by a TENCOR P-10 surface profiler.

The UV–vis absorption and luminescence spectra were respectively recorded on an HP8452A Diode Array spectrophotometer and an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature. The current and luminescence intensity as a function of applied field were measured using an assembly consisting of a PC-based DC power supply (HP 6623A) and a digital multimeter (HP 34401). A light power meter (Newport Instruments, Model 818-UV) was used to measure the device light output in microwatts. Luminance was measured by a MINOLTA LS-100 luminance meter. The ultraviolet photoelectron spectroscopy (UPS) data were acquired at room temperature with a VG ESCALab 220i spectrometer (UK) with a VG UV lamp. UPS analysis was performed using He I (21.2 eV) photons. The base pressure of the analysis chamber was lower than 1 × 10^{-10} Torr and the combined instrumental resolution was about 0.1 eV. Atomic force microscopy (AFM) was conducted on a AutoProbe CP (Park Scientific Instruments, USA) at the Korea University Engineering Laboratory Center, Seoul, Korea.

ITO/polymer 1/Ca/Al and ITO/PEDOT/polymer 1/Ca/Al devices. The patterned ITO-coated glass slides were cleaned by sequential ultrasonication in acetone, propan-2-ol and distilled water for 13 minutes, respectively, and finally cleaned by ultraviolet–ozone for 13 minutes.[34]

The conducting polymer solution of poly(3,4-ethylenedioxythiophene-2,5-diyl) doped with polystyrene sulfonate (PEDOT–PSS) (Bayer) was spin-coated with 3300 rpm for 1 min and dried at 150 °C for 30 minutes. The electrical conductivity of this film measured by the four line probe method was 10 S $\mathrm{cm^{-1}}$. The solution (1 wt%) of polymer **1** in purified 1,1,2,2-tetrachloroethane[30] was spin-coated at 1000 rpm for 1 min and the film was subjected to thermal treatment at 150 °C for 1 h under vacuum. The Ca cathode 2000 Å thick was vacuum deposited from the tungsten boat at a deposition rate of 2 Å $\mathrm{s^{-1}}$ under a pressure of 3.0×10^{-7} Torr. An Al capping layer was then evaporated to protect the Ca cathode at a deposition ratio of 4 Å $\mathrm{s^{-1}}$ under the same pressure. The active area of the EL devices was 4 $\mathrm{mm^2}$.

Photoluminescence (PL) and electroluminescence (EL) spectra were recorded on a PC1 photon counting spectrofluorometer (ISS Inc., USA). Current–voltage (*I–V*) characteristics and the intensities of EL emission were simultaneously measured with a Keithley 238 SMU electrometer and a BM7 luminance meter (Topcon Technologies, Inc., USA). Device fabrication and all the measurements were performed in a dry argon filled glove box without exposing to air.

Results and discussion

Synthesis of monomers and polymers

Polymers **1** and **2** were synthesized by the Gilch and Wheelwright method[33] widely used in the synthesis of organic soluble PPV derivatives. The structures of intermediates and monomers were confirmed by elemental analysis, and IR and ^{1}H-NMR spectroscopy.

Polymer **1** is readily soluble at room temperature in organic solvents such as tetrahydrofuran and 1,1,2,2-tetrachloroethane. However, polymer **2** shows a poorer solubility in these solvents. The molecular weight of polymer **1** determined by gel-permeation chromatography in tetrahydrofuran against a polystyrene standard is $\bar{M}_w = 72\,000$ and $\bar{M}_w = 49\,700$ with a polydispersity index (PDI) of 1.4. The relatively narrow molecular weight distribution must be brought about by removal of the low molar mass portion by the extraction process. Since polymer **2** is not readily soluble in solvent, we measured only its solution viscosity values at 30 °C for a solution (0.2 g $\mathrm{dL^{-1}}$) in 1,1,2,2-tetrachloroethane; its solution inherent viscosity value is 1.12 dL $\mathrm{g^{-1}}$. Both polymers readily form free standing films when cast from 1,1,2,2-tetrachloroethane solution.

UV–vis absorption and photoluminescence characteristics

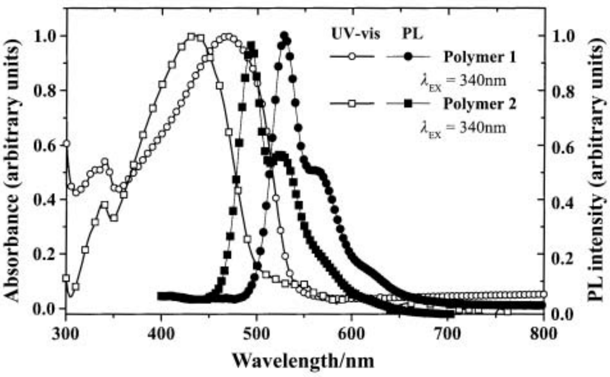


Fig. 1 UV–vis absorption and PL spectra of thin films of polymers **1** and **2** ($\lambda_{\mathrm{EX}} = 340$ nm).

Fig. 1 compares UV–vis absorption spectra and photoluminescence (PL) spectra of polymers **1** and **2**. Both polymers **1** and **2** show an absorption from the carbazole moiety with $\lambda_{\max}$ at 340 nm. For polymer **1** the absorption at 350–540 nm originates from the π–π* transition of the main chain. Polymer **2** absorbs at about 350–500 nm for the same transition. The red-shift for the absorption by polymer **1** when compared to polymer **2** can be explained by the presence of the electron donating alkoxy pendant group, since the alkoxy group is well known to be an electron donor.[35,36] The absorption edges of the absorption spectra for polymers **1** and **2** are 530 and 500 nm, respectively, corresponding to the optical band gap of 2.4 eV and 2.5 eV. As is well known,[35,36] the presence of the electron-donating alkoxy groups in polymer **1** reduces the band gap energy when compared with polymer **2** which does not bear the alkoxy pendants. These values are very close to the value (2.4 eV) of PPV reported earlier by others[37] and us.[8] The absorption positions by the carbazole pendant groups in the polymers are slightly red-shifted when compared with the absorption position of the corresponding low molar mass compound. Carbazole itself shows absorption at 300–345 nm in ethanol with $\lambda_{\max} = 323$ nm.[38] This suggests that there is a slight electronic interaction between the main chain and the carbazole pendant. Similar observations were made by us earlier for the PPV derivatives carrying styryl pendants.[39] When compared with the absorption of unsubstituted PPV ($\lambda_{\max} = 430$ nm), the absorption ($\lambda_{\max} = 461$ nm) by polymer **1** is red-shifted whereas the absorption ($\lambda_{\max} = 433$ nm) position by polymer **2** is similar to PPV. Poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) absorbs at 350–570 nm with $\lambda_{\max} = 503$ nm. The only structural difference between polymer **1** and MEH-PPV is that polymer **1** bears a carbazole moiety instead of the methoxy group in MEH-PPV. The carbazole group appears to be less efficient in electron-donating than the methoxy group according to the UV–vis absorption spectra of polymer **1** and MEH-PPV. In fact, comparison of the UV–vis absorption spectrum of polymer **2** with that of PPV leads to the conclusion that the carbazole group causes little change in the absorption position. It is conjectured that the electron-donation character of the carbazole group is nullified by the partial destruction of the coplanarity of the main chain by the steric effect brought about due to its bulkiness.

Photoluminescence (PL) spectra of the films (600 nm thick) of polymers **1** and **2** obtained for the excitation wavelength of 340 nm are compared in Fig. 1. Polymer **1** emits light between 490–650 nm (maximum emission at about 530 nm) and polymer **2** at 450 nm–630 nm (maximum emission at about 490 nm). The PL emission of polymer **1** again is red-shifted when compared with the emission by polymer **2**. The PL spectra of polymers **1** and **2** are composed of two main bands, being slightly simpler than the spectral feature of PPV emission.

In fact, the general feature of the emission spectra of polymer **1** and **2** is very similar to that of MEH-PPV. The strongest emission peaks of the present polymers may be the results of overlapped emissions both by the carbazole pendants and the alkoxy-substituted (polymer **1**) or unsubstituted (polymer **2**) main chain. Alternatively carbazole groups may be involved only in energy transfer processes between themselves and the backbone. Carbazole itself emits light over 340–420 nm in ethanol.[38] Poly(vinylcarbazole) is known to emit at 360–540 nm with maximum emission at 418 nm.[3] The excitation spectra of polymer **1** collected for the emission at the wavelengths of 530, 560, and 620 nm are given in Fig. 2 and are compared with its absorption spectrum. First of all, we note not only that the excitation spectra are independent of emission

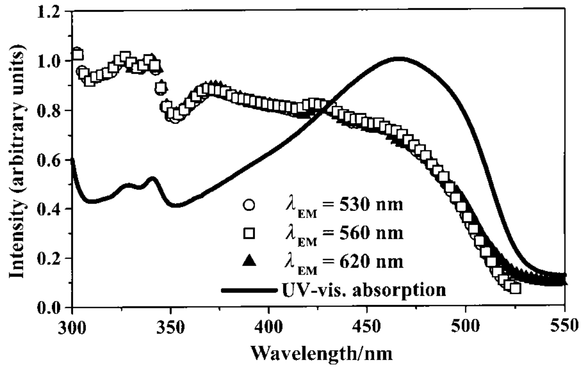


Fig. 2 Comparison of excitation spectra of polymer **1** at different emission wavelength.

wavelength and are not exactly same as the absorption spectrum, but also that absorption by the carbazole pendants at about 320–350 nm makes a strong contribution to the emission by the backbone, which can be interpreted by a facile excited state energy transfer from pendants to the backbone. This must be the reason why we do not observe the occurrence of a separate emission by the carbazole pendants. Lee *et al.*[40] recently reported a similar energy transfer process for poly(carbazolylacetylenes). If this is the case, the emission peaks should not contain the contribution from the carbazole pendants and they are mainly from the π-systems in the main chain. In addition, we observed that the PL spectra of polymers **1** and **2** show exactly the same features regardless of the excitation wavelength, indicating that the emissive state is the same even with high-energy excitation.

Electroluminescence and *I–V* characteristics of light-emitting devices

Fig. 3 compares electroluminescence (EL) and photoluminescence (PL) spectra of polymers **1** and **2**. The general appearance of the EL spectra is not much different from the corresponding PL spectra with the EL spectra being broader. It implies that the carbazole moiety just changes the electronic state of the main chain and does not emit light. This also indicates that emissive excitons are formed from combination of the injected holes and electrons mainly along the main chain, and if any excitons are formed in the pendants, they are in a higher energy state and, thus, migrate very fast to the lower energy states of the main chain.

The characteristics of current density and light intensity *versus* electric field of ITO/polymer **1** or **2**/Al devices are compared in Fig. 4. The threshold field required to obtain a current density of 0.1 mA mm^{-2} for polymer **1** was 0.6 MV cm^{-1} and is lower than that of polymer **2** (0.8 MV cm^{-1}). These *I–V* characteristics could be explained using a band–bend model where the carriers are injected through triangular barriers caused by the offset between the bands of the polymer and the electrode.[41] We obtained energy levels of polymers **1** and **2** from ultraviolet photoelectron spectra (UPS)[8] and their optical band gaps. The HOMO and LUMO energy levels of polymers were evaluated as described by Schmidt *et al.*[42] The HOMOs of polymers **1** and **2** are 5.5 and 6.1 eV, respectively. Their LUMO levels were evaluated to be 3.2 and 3.6 eV, respectively. In general, the LUMO level of a PPV derivative is significantly lowered by the alkoxy group attached to the phenylene ring as is observed for the present polymers.[35,36] According to the band diagram it is expected that injection of holes from the ITO anode to polymer **1** will be more favorable than to polymer **2**. This indicates that, at the same field, the current density of polymer **1** will be higher than that of polymer **2** as shown in Fig. 4. As a result the field required to obtain the same current density is lower for polymer **1** than for polymer **2**. The inset in Fig. 4 also tells us that the brightness of emitted light by polymer **1** increases much more rapidly than that by polymer **2**.

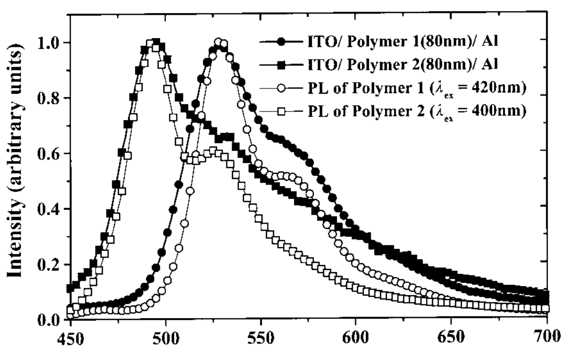


Fig. 3 Comparison of EL and PL spectra of polymer **1** and **2**.

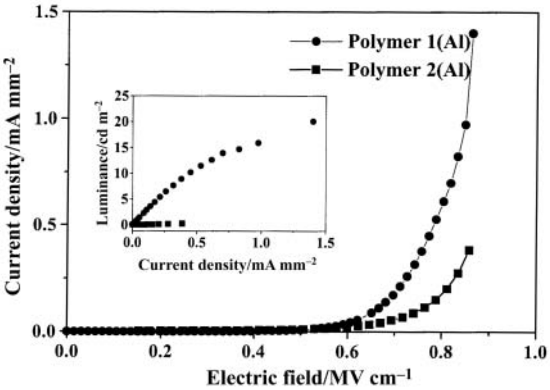


Fig. 4 Comparison of electric field *vs.* current density and light intensity (inset) curves of ITO/polymer **1** or **2** (60 nm)/Al devices.

The external quantum efficiencies of the devices fabricated from the two polymers are compared in Fig. 5. For the sake of comparison, data for PPV and MEH-PPV prepared by us[8] are included in Fig. 5. The maximum external quantum efficiency of the ITO/polymer **1**/Al device is 0.01% and is 550-fold higher than that of the ITO/polymer **2**/Al device (1.8 × 10^{-5}%), and 60-fold higher than ITO/PPV/Al (1.7 × 10^{-4}%). This value is about 5.6 times the efficiency reported for MEH-PPV devices.[41] The higher external quantum efficiency of polymer **1** than that of polymer **2** may partly be due to an improved balance of the carrier injection and transport. Also, it is probable that the bulky alkoxy pendant groups in polymer **1** keep the conjugated polymer backbones apart from each other and prevent the formation of interchain excitons more efficiently than polymer **2**.[24,25] Formation of interchain excitons is known to cause

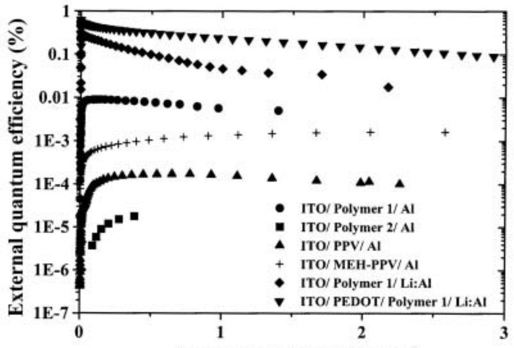


Fig. 5 Comparison of external quantum efficiencies of polymer **1**, **2** and PPV devices.

nonradiative decay lowering the external quantum efficiency of LED devices.[26–28] As a result of these factors, it seemed that polymer **1** shows a much higher efficiency than polymer **2**.

Moreover, it was noted that the film quality of polymer **1** was much better than polymer **2**. Spin-casting of polymer **1** gave a film of an average roughness of 12.4 Å, whereas the average roughness (29.2 Å) of the polymer **2** film was much worse. The difference results from poorer solubility of polymer **2** in organic solvents than polymer **1**. In addition, our preliminary results[43] suggest that polymer **1** may reveal an improved balance in carrier transport, which would result in a better EL device performance.

Fig. 5 also shows that a device prepared using a Li : Al alloy exhibits much higher external efficiencies than the ones having the Al cathode. Evidently, the low work function of lithium metal (2.9 eV) improves electron injection.[44] In addition, insertion of the conducting PEDOT [poly(3,4-ethylenedioxy-2,5-thiophene)] layer between the ITO anode and the light emitting layer further improves the efficiency.[45] Fig. 5, however, implies that the devices with the Li cathode have a poor stability. This may be due to the higher sensitivity of the lithium metal toward air including water, oxygen and carbon dioxide. It is also very possible that aluminium was not effectively co-deposited to protect the lithium metal. The presence of the conducting layer did not change the EL spectrum at all in the overall position and shape. This is a strong indication that the conducting layer simply acts as a carrier transporting medium.

In order to facilitate carrier injection, in addition to the use of a conducting polymer layer on the ITO electrode, we fabricated a device using a low work function calcium cathode instead of aluminium. We again coated the doped PEDOT layer, as an organic conducting hole injection layer, on the ITO electrode. It not only makes the hole injection easier, but also is expected to mitigate the adhesion problem between the electrode and organic emitting layer.[46] In order to protect the calcium cathode, aluminium was vacuum deposited onto it. We compared the characteristics of two LED devices; ITO/polymer **1**/Ca/Al (device **A**) and ITO/PEDOT/polymer **1**/Ca/Al (device **B**). The electric field *versus* current density and light intensity characteristics of devices are compared in Fig. 6. For the sake of comparison, data for the device fabricated using MEH-PPV prepared by us also are included in the figure.

It is known that[23] the major carrier for PPV and its derivatives is positive holes that govern the threshold electric field and that minor carriers are electrons that control the device efficiency. As described above, the PEDOT layer (see Fig. 6a) helps hole (major carrier) injection to the polymer layer and reduces turn-on electric field of device **B** (0.31 MV cm^{-1}) compared to device **A** (0.43 MV cm^{-1}). Because the Ca cathode facilitates electron injection to the emitting polymer layer, the balance of electron and hole injection could be improved and the radiationless quenching of excitons at the metal electrode/polymer interface could be reduced by shifting the recombination zone away from the metal electrode.[47,48]

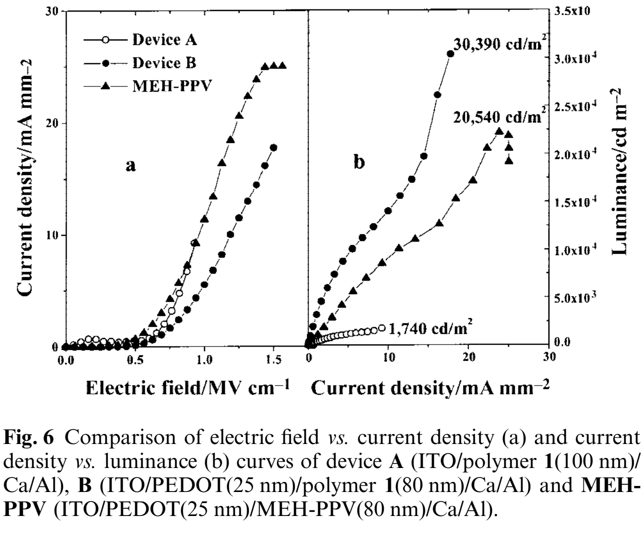


Fig. 6 Comparison of electric field *vs.* current density (a) and current density *vs.* luminance (b) curves of device **A** (ITO/polymer **1**(100 nm)/Ca/Al), **B** (ITO/PEDOT(25 nm)/polymer **1**(80 nm)/Ca/Al) and **MEH-PPV** (ITO/PEDOT(25 nm)/MEH-PPV(80 nm)/Ca/Al).

As a result, the external quantum efficiencies of the devices **A** and **B** are significantly higher than that of the ITO/polymer **1**/Al device. Fig. 6b clearly demonstrates that device **B** performs best among the three devices as far as brightness of emitted light and photometric efficiency are concerned. The device fabricated from polymer **1** and PEDOT exhibits the highest luminance for the same current density values. This tells us that opposite carriers form singlet excitons most effectively in device **B** indicating that injection and mobility of the carriers are most balanced. The maximum photometric efficiencies of devices **A** and **B** were 0.3 and 4.4 cd A^{-1}, respectively, with the maximum luminance attainable being 1740 cd m^{-2} for device **A** at an electric field of 1.0 MV cm^{-1} and 30 390 cd m^{-2} for device **B** at an electric field of 1.50 MV cm^{-1}. The device fabricated with MEH-PPV showed a maximum photometric efficiency of 1.1 cd A^{-1} with the maximum luminance being 20 540 cd m^{-2} at 1.38 MV cm^{-1}. The driving electric fields for 200 cd m^{-2} were 0.59 MV cm^{-1} for device **A** and 0.45 MV cm^{-1} for device **B**, respectively. In comparison, the maximum luminance value observed for the devices of ITO/polymer **1**/Li : Al was 1300 cd m^{-2}. It also should be noted that polymer **1** is a green light emitter whereas MEH-PPV is an orange–red light emitter. As far as device stability is concerned, it took 70 hours for the device **B** to reduce its brightness from 1000 cd m^{-2} to 500 cd m^{-2}. However, detailed studies are required on the long-term stability of the devices described.

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