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Synthesis and electroluminescence of poly(aryleneethynylene)s based on fluorene containing hole-transport units

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A new series of light-emitting poly(aryleneethynylene)s (PAE) based on fluorene with sterically hindered substituents containing hole transport units such as tetraphenyldiaminobiphenyl, carbazole and thiophene and the non-planar unit binaphthyl were synthesized by a palladium-catalyzed coupling reaction. The introduction of hole transport moieties into the PAE main chain can improve the luminance properties of PAE type polymers. The electronic structures and photo- and electroluminescent (EL) properties of these polymers can be manipulated by simply varying the nature of the co-units in the polymeric chain. The spectral emission varies from greenish-blue to green or yellowish-green, depending on the composition of the copolymers. A single-layer light-emitting diode (LED) prepared from poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-[*N,N*′-diphenyl-*N,N*′-bis(4-phenyl)-1,1′-biphenyl-4,4′-diamine]} (TPD-PFE) using an aluminium electrode emits green light (510 nm) with an EL external quantum efficiency of 0.007% and a brightness of 30 cd m^{-2} at a bias voltage of 27 V and a current density of 420 mA cm^{-2}. An EL external quantum efficiency of 0.06% can be obtained from a blue-emitting double-layer LED with the structure of ITO/TPD-PFE/2-(2-hydroxyphenyl)pyridylberyllium/LiF/AlLi at a current density of 38 mA cm^{-2}.

Introduction

Poly(aryleneethynylene)s (PAEs) are rigid-rod conjugated materials composed of aromatic rings and alkyne functions. The high fluorescence quantum yield and excellent stability of PAE polymers make these materials another class of prospective materials for photoluminescence (PL) applications.[1–3] Weder *et al.* reported incorporation of the PL material poly(2,5-dialkoxy-*p*-phenyleneethynylene) into liquid crystal displays to simplify device design and substantially increase device brightness, contrast, efficiency and viewing angle.[4,5] Although the electroluminescence (EL) of PAEs has been studied for a few systems, for example, poly(phenyleneethynylene)s, there is not much satisfaction with the performance of EL devices,[6–10] so PAEs are generally not considered to be a promising material for EL applications.[11] The poor performance of the devices fabricated with PAE is ascribed to charge imbalance between electrons and holes since most PAE polymers are more favorable to electron injection than to hole injection due to the electron-withdrawing effect of the -C≡C- group.[12] Another factor related to low EL efficiency is aggregate formation due to the rigid-rod conformation of the PAE main chain resulting in a reduction of the radiative recombination efficiency.[13]

Fluorene derivatives show interesting and unique chemical and physical properties because they contain a rigid planar biphenyl unit and the facile substitution at the remote C9 position can improve the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone.[14,15] As a result, polyfluorenes have emerged as the most attractive blue-emitting materials due to their high efficiency and good thermal stability.[16–23]

In this paper, first of all, a fluorene moiety with sterically hindered substituents is introduced into the PAE main chain to improve the EL efficiency and thermal stability of PAEs. Secondly, a hole transport moiety such as tetraphenyldiaminobiphenyl (TPD), carbazole and thiophene is incorporated into the PAE backbone to achieve balanced mobility of both charge carriers. Finally, binaphthyl and thiophene units are introduced into PAEs to reduce the rigid-rod conformation and to improve the processability of the materials taking advantage of the bent bond angles at 2,5-thienylene[24] and of the large dihedral angle at binaphthyl.[25] Thus, we report the synthesis of a new series of PAEs based on fluorene and demonstrate that the strategy given above can improve the performance of light-emitting diodes (LED).

Experimental

Chemicals

Only analytical grade quality chemicals were used. Triethylamine was dried over CaH_2 and distilled under N_2 atmosphere prior to use, and toluene was dried with sodium–benzophenone. The catalyst tetrakis(triphenylphosphine)palladium(0)[26] was synthesized according to the literature method. The monomers such as 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene,[27] 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene,[27] *N,N*′-diphenyl-*N,N*′-bis(4-bromophenyl)-1,1′-biphenyl-4,4′-diamine,[27] 3,6-diiodo-9-hexylcarbazole,[28] 2,5-diiodothiophene,[29] 1,4-diiodo-2,5-bis(hexyloxy)benzene[1] and 6,6′-dibromo-2,2′-bis(hexyloxy)-1,1′-binaphthyl[30] were prepared by literature procedures.

Instrumentation

FT-IR spectra were taken on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer with KBr pellets. UV-Vis spectra were

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recorded on a General TU-1201 UV-Vis spectrophotometer. ^{1}H NMR spectra were obtained in chloroform-*d* on a Bruker dmx 300 NMR spectrometer and the spectral data are expressed on the δ scale relative to tetramethylsilane as internal standard. Elemental analyses were carried out on a Carlo Erba Model 1106 elemental analyzer. Thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer Series 7 thermal analysis system under N_2 at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 under N_2 at a heating rate of 20 °C min^{-1}. The weight-average molecular weight (M_w) and polydispersity indices (M_w/M_n) of polymers were measured on a PL-GPC Model 210 chromatograph at 35 °C, using THF as eluent and standard polystyrene as reference.

Synthesis of polymers

The synthetic route to the polymers is illustrated in Scheme 1.

Poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-(9-hexyl-3,6-carbazole)} Cz-PFE. A mixture of 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene (**1**) (438 mg, 1.0 mmol) and 3,6-diiodo-9-hexylcarbazole (**4**) (503 mg, 1.0 mmol) in triethylamine (20 mL) and toluene (40 mL) was degassed for 30 min. $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added. After the reaction mixture was refluxed under nitrogen for 48 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was dissolved in a minimum amount of $CHCl_3$ and then poured into methanol to give a precipitate. The obtained solid was redissolved in $CHCl_3$ and reprecipitated from methanol, followed by Soxhlet extraction with the same solution for 24 h to give an orange powder (604 mg, 88%). Anal. Calcd for $(C_{51}H_{59}N)_n$: C, 89.29; H, 8.67. Found: C, 88.55; H, 8.89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 2H), 7.82–6.91 (m, 10H), 4.17 (t, 2H), 2.22–1.70 (m, 6H), 1.27 (m, 8H), 1.15–0.40 (m, 31H). FT-IR (KBr): 2960, 2927, 2857, 1594, 1466, 1379, 1262, 1095, 1023, 866, 804, 699 cm^{-1}.

Poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-[2,5-bis(hexyloxy)benzene]} Ph-PFE. Ph-PFE was prepared by a procedure similar to that of Cz-PFE, using 1,4-diiodo-2,5-bis(hexyloxy)benzene (**6**) instead of **4**; the product was isolated as a yellow solid in 80% yield (570 mg). Anal. Calcd for $(C_{51}H_{68}O_2)_n$: C, 85.90; H, 9.61. Found: C, 85.42; H, 9.56%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.00 (m, 8H), 3.97 (t, 4H), 2.04 (d, 4H), 1.82 (m, 4H), 1.58–1.17 (m, 14H), 1.10–0.40 (m, 34H). FT-IR (KBr): 2959, 2926, 2872, 2857, 1645, 1605, 1490, 1465, 1379, 1262, 1098, 1024, 804, 741, 697 cm^{-1}.

Poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-(6,6′-[2,2′-bis(hexyloxy)-1,1′-binaphthyl])} BN-PFE. BN-PFE was prepared by a procedure similar to that of Cz-PFE, using 6,6′-dibromo-2,2′-bis(hexyloxy)-1,1′-binaphthyl (**7**) instead of **4**; the product was isolated as a yellow solid in 90% yield (800 mg). Anal. Calcd for $(C_{65}H_{76}O_2)_n$: C, 87.79; H, 8.61. Found: C, 88.24; H, 8.59%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2H), 7.83 (d, 2H), 7.68 (d, 2H), 7.50 (dd, 4H), 7.43 (d, 2H), 7.27 (dd, 2H), 6.97 (d, 2H), 4.00–3.81 (m, 4H), 2.15 (d, 4H), 1.55–1.20 (m, 18H), 1.10–0.40 (m, 34H). FT-IR (KBr): 2961, 2927, 2871, 2857, 1614, 1588, 1490, 1464, 1262, 1097, 1025, 871, 804, 695 cm^{-1}.

The synthesis of poly[9,9-bis(2-ethylhexyl)fluoren-2,7-ylene-ethynylene] (PFE),[27] poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-[*N,N*′-diphenyl-*N,N*′-bis(4-phenyl)-1,1′-biphenyl-4,4′-diamine]} (TPD-PFE)[27] and poly{[2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene]-*alt*-(2,5-thienylene)} (Th-PFE)[31] was reported in our previous papers.

Cyclic voltammetry (CV) measurements

For studies of electrochemical behavior, a polymer thin film was prepared on a platinum wire as a working electrode, using a platinum wire as the counter electrode and Ag/Ag$^+$ as the reference electrode in a solution of tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile. Cyclic voltammograms were recorded on a computer controlled EG&G Potentiostat/Galvanostat Model 283.

LEDs fabrication and PL and EL measurements

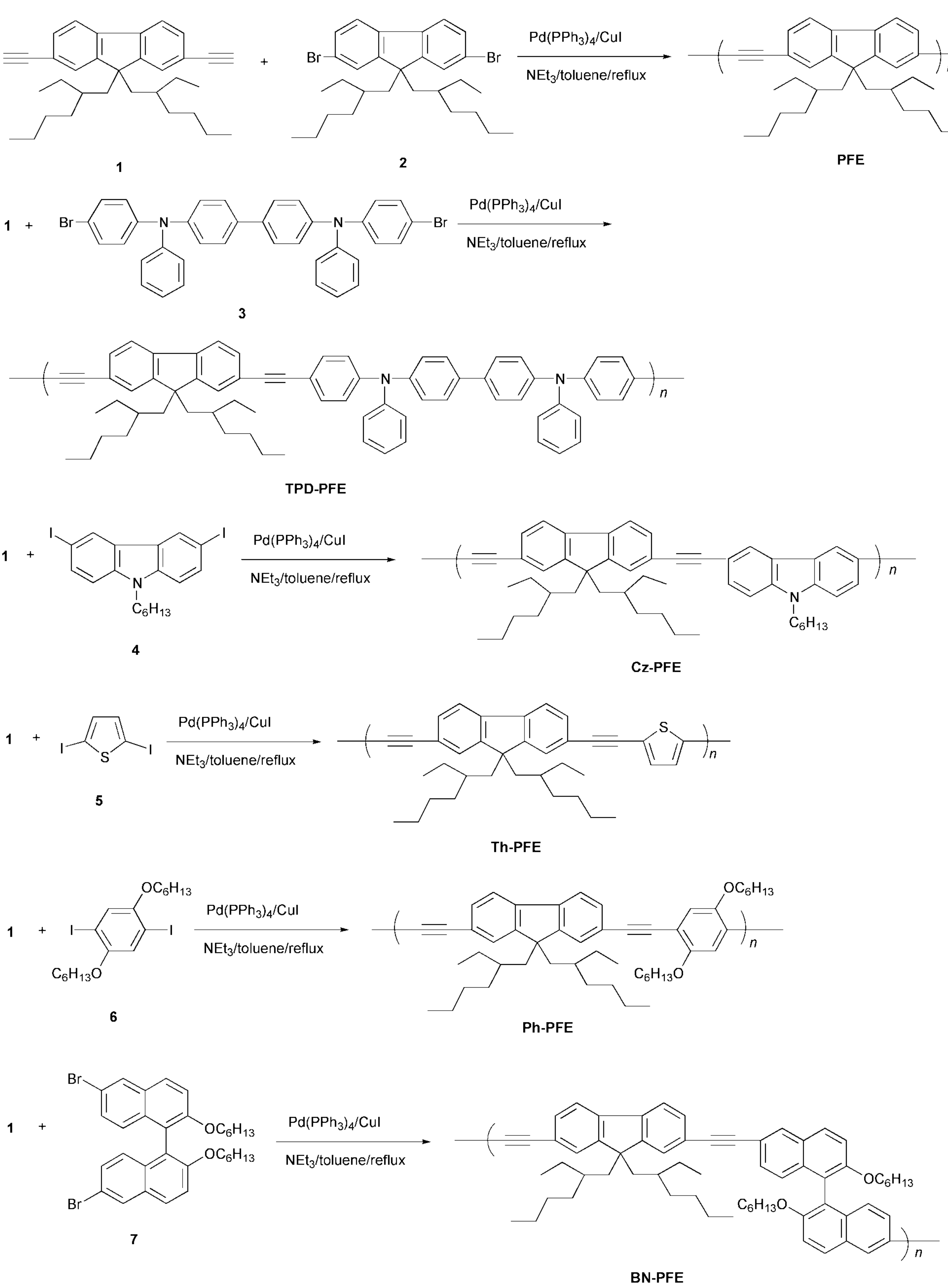
Single-layer LEDs were prepared by spin-coating a TPD-PFE solution in chloroform onto glass substrates covered by patterned indium tin oxide (ITO) electrodes, LiF was vacuum-deposited as insulating layer, and an aluminium electrode was deposited on the top of the device at below 1×10^{-6} Torr. For double-layer devices, a thin polymer film was spin-coated as the hole transport layer from a filtered 2.0 wt% of TPD-PFE solution in chloroform on ITO substrates. 2-(2-Hydroxyphenyl)pyridylberyllium ($BePP_2$)[32] was vacuum-deposited as the electron transport layer. LiF was vacuum-deposited as insulating layer, and an aluminium/lithium alloy electrode was deposited on the top of the device at below 1×10^{-6} Torr. Double-layer LEDs with the structure ITO/copper phthalocyanine (CuPc)/polymer/Ca/Ag were fabricated. The CuPc, Ca and Ag layers were evaporated under vacuum (10^{-6} Torr). Thin films of the polymers were spin-coated from $CHCl_3$ solution at 2000 rpm for 20 s. The thicknesses of CuPc and the polymers were ~20 and ~75 nm, and the active areas of the resulting devices were 6.16 mm^2. All device testing was carried out in air at room temperature. PL spectra of the polymers in chloroform solutions and thin films on quartz substrates and EL spectra of forward biased LEDs were recorded with an Oriel InstaSpec IV charge coupled device camera. Current–voltage characteristics were measured on a Hewlett Packard 4155B semiconductor parameter analyzer. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Photometric units (cd m^{-2}) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission.[33]

Results and discussion

The obtained polymers are soluble in common organic solvents, such as chloroform, tetrahydrofuran (THF) and toluene. This is partially due to the 2-ethylhexyl side chain attached to the fluorene moiety. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) with THF as eluent and polystyrene as the standard. Ar-PFE type polymers have weight average molecular weights (M_w) of 16 000–23 000 with polydispersity indices (M_w/M_n) of 2.0–2.8 (see Table 1). The thermal properties of the six polymers were determined by TGA and DSC. The six polymers possess good thermal stability with onset decomposition temperature (T_d) of 370–400 °C and glass transition temperature (T_g) of 65–93 °C as shown in Table 1.

Oxidation and reduction waves were revealed for TPD-PFE (Fig. 1), which implies that it has the capability for transporting both electron and hole. It is important to note that when 2,7-diethynylfluorene and TPD units are linked alternately by a sigma bond, the two moieties keep their own electrochemical characteristics intact. On sweeping the polymer cathodically, the onset of the reduction occurs at about −2.46 V above which the cathodic current quickly increases, and a cathodic peak appears at −2.76 V. For oxidation, the onset potential is 0.42 V and an anodic peak occurs at 0.58 V.

The redox potentials *vs.* Ag/Ag$^+$ and the band gaps of the six polymers are summarized in Table 2. The oxidation potentials



Scheme 1 Synthetic route to the polymers.

of the polymers TPD-PFE, Cz-PFE and Th-PFE are 0.42, 0.62 and 0.63 V, respectively. The introduction of electron-donating segments TPD, carbazole and thiophene leads to a significant reduction in oxidation potentials from the value of 0.72 V for the poly(fluorenyleneethynylene) homopolymer, PFE, which indicates that the hole transporting ability of these polymers is enhanced. The band gaps of all polymers are estimated from the onset positions of the absorption bands to be 2.67–2.90 eV.

The photophysical characteristics of the polymers were investigated in solution and in the solid state. The absorption and emission data for the six polymers in solutions and in the films cast from solution in $CHCl_3$ are summarized in Table 3. The absorption spectra of the six polymers obtained for diluted $CHCl_3$ solutions are shown in Fig. 2. All polymers show the maximum absorptions in the range 300–350 nm. The absorption spectrum of TPD-PFE in the solution is red-shifted in

Table 1 Molecular weights and thermal properties of Ar-PFE polymers

Ar	Yield/%	M_w[a]	M_w/M_n[a]	T_d[b]/°C	T_g[c]/°C
—	82	19 200	2.53	381	65
TPD	85	17 600	2.81	388	75
Cz	88	22 500	2.04	371	89
Th	86	19 700	2.26	398	79
Ph	80	23 300	2.34	385	72
BN	90	15 800	2.08	398	93

[a] Molecular weights and polydispersity indices determined by GPC in THF on the basis of polystyrene calibration. [b] Onset decomposition temperature measured by TGA under N_2. [c] Glass transition temperature measured by DSC under N_2.

comparison with those for other polymers. Such a red shift could be attributed to the intrachain charge transfer.[34] The absorption spectrum of TPD-PFE in the solid state is slightly red-shifted relative to that in the solution. The absorption spectra of other polymers in chloroform solutions are almost identical to those in thin films.

All polymers in chloroform solutions emit blue fluorescence under ultraviolet irradiation. The PL spectra in the solutions, which are attributed to fluorescence because of the short lifetime of the excited state,[35] show blue emissions around 420–470 nm as shown in Fig. 3. The PL spectra of the copolymers in solutions are red-shifted relative to that for the homopolymer. The thin films of the six polymers show greenish-blue, green and greenish-yellow emissions around 495–540 nm, depending on the composition of the copolymers (Table 3). The PL spectra in solid states are red-shifted relative to those in solutions. Such red shifts could be attributed either to the difference in energy transfer processes between film and solution due to the presence of rotational conformers in the solution reducing the conjugation of the chromophore, or to the effect of packing and local geometry of the polymers.[36]

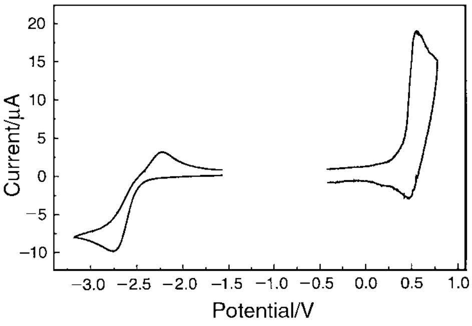


Fig. 1 Cyclic voltammograms of TPD-PFE recorded from a thin film deposited on a platinum wire electrode at a scan rate of 40 mV s^{-1}. The potentials were measured relative to the Ag/Ag^+ reference electrode.

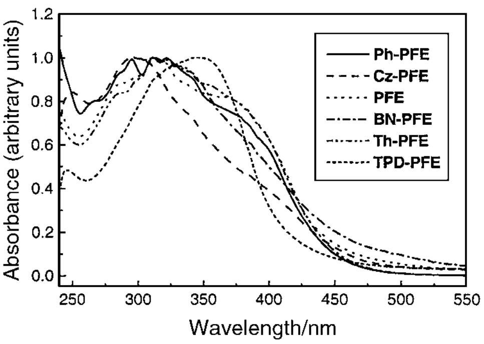


Fig. 2 Absorption spectra of the polymers in chloroform solution.

Table 2 Redox potentials and band gaps of the six polymers

Polymer	E_ox[a]/V	E_red[b]/V	E_g[c]/eV
PFE	0.72	−2.14	2.76
TPD-PFE	0.42	−2.46	2.90
Cz-PFE	0.62	−2.21	2.67
Th-PFE	0.63	−2.20	2.70
Ph-PFE	0.84	−2.12	2.71
BN-PFE	0.66	−2.26	2.68

[a] Onset oxidation potential *vs.* Ag/Ag^+. [b] Onset reduction potential *vs.* Ag/Ag^+. [c] Band gaps estimated from the onset position of the absorption bands.

Table 3 Absorption and emission data for the six polymers

	Absorption λ_max/nm		PL λ_max/nm	
Polymer	In $CHCl_3$	In film	In $CHCl_3$	In film
PFE	313	312	424	530
TPD-PFE	347	358	444	495
Cz-PFE	297	300	470	525
Th-PFE	312	311	447	519
Ph-PFE	312	312	444	524
BN-PFE	312	312	455	540

Single-layer devices were fabricated with ITO as the anode, Al as the cathode, LiF as the insulating layer, and TPD-PFE as the emissive layer. The EL spectrum of the single-layer LED is shown in Fig. 4. EL of TPD-PFE peaks at 510 nm, which is 15 nm red-shifted relative to PL of the polymer in the solid film. In the previous literature, the devices assembled with PAE polymers as emissive layers were reported to emit yellow-green to yellow light, and the emission center may be aggregate or excimer.[3] It is worth noticing that green emission was observed from the LED prepared with TPD-PFE as emissive material, which may be ascribed to suppression of aggregate formation because of

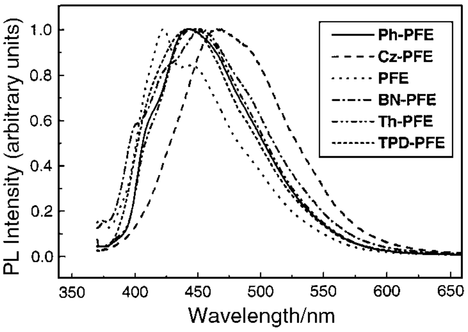


Fig. 3 PL spectra of the polymers in chloroform solution.

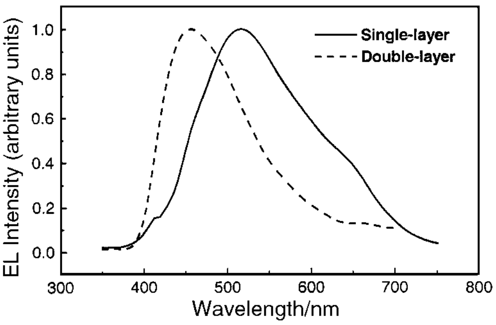


Fig. 4 EL spectra of ITO/TPD-PFE/LiF/Al and ITO/TPD-PFE/$BePP_2$/LiF/AlLi.

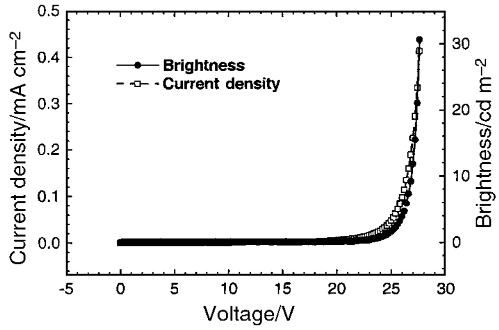


Fig. 5 *I–V–B* characteristics of an ITO/TPD-PFE/LiF/Al device.

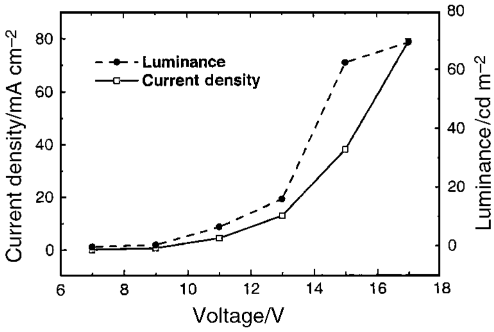


Fig. 6 *I–V–B* characteristics of an ITO/TPD-PFE/BePP$_2$/LiF/AlLi device.

the introduction of two sterically hindered 2-ethylhexyl groups. Fig. 5 shows the current–voltage–brightness (*I–V–B*) characteristics for the single-layer LED. An EL external quantum efficiency of 0.007% and brightness of 30 cd m^{-2} can be obtained at a bias voltage of 27 V and a current density of 420 mA cm^{-2}. Double-layer devices were fabricated with ITO as the anode, AlLi alloy as the cathode, LiF as the insulating layer, TPD-PFE as the hole transport layer, and BePP$_2$ as the electron transport layer. Fig. 4 shows the EL spectrum of the double-layer LED. A broad EL emission from 400 to 650 nm with a maximum at 456 nm and a unresolved shoulder at *ca.* 500 nm was observed, which is different from the PL spectra in solid states with the emission maxima locating at 450 (BePP$_2$)[32] and 495 nm (TPD-PFE). This suggests that the blue emission comes mainly from the radiative decay of the singlet excitons at the interface formed by the recombination of holes and electrons injected from the TPD-PFE and BePP$_2$ layers, respectively. Fig. 6 presents the brightness–voltage (*B–V*) and current–voltage (*I–V*) characteristics of ITO/TPD-PFE/BePP$_2$/LiF/AlLi. The device has a turn-on voltage of 7 V, EL external quantum efficiency of 0.06% at a current density of 38 mA cm^{-2} and brightness of 70 cd m^{-2} at a bias voltage of 17 V and a current density of 80 mA cm^{-2}.

Double-layer devices were fabricated with ITO as the anode, Ca/Ag as the cathode, CuPc as the hole transport layer, and Th-PFE as the emissive layer. The turn-on voltage of ITO/CuPc/Th-PFE/Ca/Ag was determined to be 11 V. The EL external quantum efficiency is 0.01% at a voltage of 19 V and a current density of 23.7 mA cm^{-2}. The brightness reaches 14 cd m^{-2} at a voltage of 23 V. For comparison, we prepared a double-layer device with the same structure of ITO/CuPc/PFE/Ca/Ag using the homopolymer PFE as the emissive layer. However, the performance of this device is poor because the brightness is only 1.5 cd m^{-2} at a voltage of 19.5 V. Clearly, introduction of hole transport segment into the PAE main chain can improve the luminance properties of PAE type polymers.

Conclusion

We have synthesized a novel series of conjugated PAE polymers containing hole transport units based on fluorene with sterically hindered substituents by employing a palladium-catalyzed coupling condensation reaction. The introduction of hole transport moieties into PAE main chain can improve the luminance properties of PAE type polymers. The electronic structures and EL properties of these polymers can be manipulated by simply varying the nature of the co-units in the polymeric chain. Green emission was achieved with an external quantum efficiency of 0.007% from the single-layer LED fabricated with TPD-PFE using an aluminium electrode.

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References

1 C. Weder and M. S. Wrighton, *Macromolecules*, 1996, **29**, 5157.
2 A. P. Davey, S. Elliott, O. O'Connor and W. Blau, *J. Chem. Soc., Chem. Commun.*, 1995, 1433.
3 R. Giesa, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, 1996, **C36**, 631.
4 C. Weder, C. Sarwa, A. Montali, C. Bastiaansen and P. Smith, *Science*, 1998, **279**, 835.
5 A. Montali, C. Bastiaansen, P. Smith and C. Weder, *Nature*, 1998, **392**, 261.
6 K. Yoshino, K. Tada and M. Onoda, *Jpn. J. Appl. Phys.*, 1994, **33**, L1785.
7 L. S. Swanson, J. Shinar, Y. W. Ding and T. J. Barton, *Synth. Met.*, 1993, **55–57**, 1.
8 Q. X. Ni, L. S. Swanson, P. A. Lane, J. Shinar, Y. W. Ding, S. Ijadi-Maghsoodi and T. J. Barton, *Synth. Met.*, 1992, **49–50**, 447.
9 L. S. Swanson, F. Lu, J. Shinar, Y. W. Ding and T. J. Barton, *J. Soc. Photo-Opt. Instrum. Eng.*, 1993, **1910**, 101.
10 A. Montali, P. Smith and C. Weder, *Synth. Met.*, 1998, **97**, 123.
11 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
12 T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino and K. Kubota, *Macromolecules*, 1994, **27**, 6620.
13 T. Mangel, A. Eberhardt, U. Scherf, U. H. F. Bunz and K. Müllen, *Macromol. Rapid Commun.*, 1995, **16**, 571.
14 G. Klaerner and R. D. Miller, *Macromolecules*, 1998, **31**, 2007.
15 S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765.
16 Y. Yang and Q. Pei, *J. Am. Chem. Soc.*, 1996, **118**, 7416.
17 Y. He, S. Gong, R. Hattori and J. Kanicki, *Appl. Phys. Lett.*, 1999, **74**, 2265.
18 W. Yu, Y. Cao, J. Pei, W. Huang and A. J. Heeger, *Appl. Phys. Lett.*, 1999, **75**, 3270.
19 W. Yu, J. Pei, Y. Cao, W. Huang and A. J. Heeger, *Chem. Commun.*, 1999, 1837.
20 B. Liu, W. Yu, Y. Lai and W. Huang, *Chem. Commun.*, 2000, 551.
21 D. Sainova, T. Miteva, H. Nothofer, U. Scherf, I. Glowacki, J. Ulanski, H. Fujikawa and D. Neher, *Appl. Phys. Lett.*, 2000, **76**, 1810.
22 K. Weinfurtner, H. Fujikawa, S. Tokito and Y. Taga, *Appl. Phys. Lett.*, 2000, **76**, 2502.
23 X. Jiang, S. Liu, H. Ma and A. K.-Y. Jen, *Appl. Phys. Lett.*, 2000, **76**, 1813.
24 Y. Pang, J. Li, B. Hu and F. E. Karasz, *Macromolecules*, 1998, **31**, 6730.
25 L. Zheng, R. C. Urian, Y. Liu, A. K.-Y. Jen and L. Pu, *Chem. Mater.*, 2000, **12**, 13.
26 D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
27 X. Zhan, Y. Liu, D. Zhu, W. Huang and Q. Gong, *Chem. Mater.*, in the press.

28 C. Beginn, J. V. Grazulevicius and P. Strohriegl, *Macromol. Chem. Phys.*, 1994, **195**, 2353.

29 J. M. Barker, P. R. Huddleston and M. L. Wood, *Synth. Commun.*, 1975, **5**, 59.

30 L. Ma, Q. Hu, K. Y. Musick, D. Vitharana, C. Wu, C. M. S. Kwan and L. Pu, *Macromolecules*, 1996, **29**, 5083.

31 X. Zhan, Y. Liu, D. Zhu, X. Jiang and A. K.-Y. Jen, *Synth. Met.*, in the press.

32 Y. Li, Y. Liu, W. Bu, D. Lu, Y. Wu and Y. Wang, *Chem. Mater.*, 2000, **12**, 2672.

33 N. C. Greenham, R. H. Friend and D. D. C. Bradley, *Adv. Mater.*, 1994, **6**, 491.

34 T. Yamamoto, Z. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota and S. Sasaki, *J. Am. Chem. Soc.*, 1996, **118**, 10389.

35 T. M. Swager, C. G. Gil and M. S. Wrighton, *J. Phys. Chem.*, 1995, **99**, 4886.

36 Y. Kim, S. Kwom, D. Yoo, M. F. Rubner and M. S. Wrighton, *Chem. Mater.*, 1997, **9**, 2699.