Poly(3,6-silafluorene-*co*-2,7-fluorene)-based high-efficiency and color-pure blue light-emitting polymers with extremely narrow band-width and high spectral stability[†]‡

Ergang Wang, Chun Li, Yueqi Mo, Yong Zhang, Gang Ma, Wei Shi, Junbiao Peng,* Wei Yang and Yong Cao*

Received 29th June 2006, Accepted 17th August 2006 First published as an Advance Article on the web 1st September 2006 DOI: 10.1039/b609250k

A new series of copolymers (PSiFF) based on 3,6-silafluorene and 2,7-fluorene were synthesized *via* the Suzuki polycondensation. The influences of the 3,6-silafluorene content in the copolymers on the thermal, photophysical, electroluminescence and electrochemical properties were investigated. The incorporation of 3,6-silafluorene into the polyfluorene main chain not only suppressed the long-wavelength emission but significantly improved the efficiency and color purity of the copolymer-based devices. Both fluorene and 3,6-silafluorene took part in π -conjugation of the main chain and the electroluminescence spectra were remarkably blue-shifted with increasing wide bandgap 3,6-silafluorene content. The device based on PSiFF90 with the configuration of ITO/PEDOT : PSS/PVK/polymer/Ba/Al showed a quantum efficiency of 3.34% and a luminous efficiency of 2.02 cd A⁻¹ at a brightness of 326 cd m⁻² with CIE 1931 chromaticity coordinates of (0.16, 0.07), which almost match the NTSC standard blue pixel coordinates of (0.14, 0.08). Moreover, the incorporation of 3,6-silafluorene into the polyfluorene main chain significantly improved the spectral stability at annealing. The results indicate poly(3,6-silafluorene-*co*-2,7-fluorene) could be a promising candidate for blue-emitting polymers of high efficiency and good color purity.

Introduction

Polymer light-emitting diodes (PLEDs) have attracted significant attention in both academic fields and industry because of their potential applications in large-area, flat-panel displays which can operate at relatively low driving voltages.¹ For fullcolor display applications, red, green and blue light-emitting materials (polymers, oligomers or small organic molecules) with high efficiency, color purity and stability are required.^{2,3} During the past decade, green and red (orange) light-emitting polymers have already been developed.³ Compared with green and red (orange), a good blue polymer emitter with high efficiency and good color purity remains a big challenge. Polyfluorenes (PFs) and their derivatives have evolved as a major class of blue-emitting materials for LEDs because of their high photoluminescent quantum yield, good solubility and acceptable charge carrier mobility.⁴ However, an undesired emission appearing on the long-wavelength side from 500 to 600 nm in both photoluminescence (PL) and electroluminescence (EL) of PFs not only limits the emission efficiency but damages the blue color purity.⁴ This long-wavelength emission was attributed to the formation of excimer/aggregates of polymer chains⁵ and/or the presence of quenching defects such as ketone groups on the 9-carbon of the fluorene ring formed upon oxidation.^{6,7} Although various approaches have been tried to suppress the long-wavelength emission,^{5,6,8} color purity and efficiency remain the key problems for fluorene-based blue-emitting polymers.

Most of the blue polymer emitters with high efficiency reported so far in the scientific literature show CIE coordinates (0.15, 0.20) and over.^{9,10} A typical example of this category is reported by Wu et al.¹⁰ from the Dow Chemical Company for blue-emitting polyfluorene copolymers with CIE coordinates (0.17, 0.21) and a good efficiency of 3-4 cd A^{-1} at 100–1000 cd m^{-2} , though no detailed chemical structure has been reported. Besides the efficiency, the color saturation is most important for display applications because in order to display all colors of the visible spectrum by synthesizing them from the three primary colors their respective colors have to be as saturated as possible, that is the color coordinates have to be positioned close to the borders of the color triangle.¹¹ It is ideal for the CIE coordinates of blue light-emitting polymers in practical display applications to match with CIE coordinates (0.14, 0.08) specified in the National Television System Committee (NTSC) standard. Recently, several groups reported deep-blue emitters, the CIE coordinates of which matched the NTSC standard, yet the efficiencies of the devices based on such emitters were still low.^{8c,12} For example, Miteva et al. reported end-capped polyfluorenes of good deep-blue emission with CIE coordinates (0.15, 0.08) and an efficiency of

Institute of Polymer Optoelectronic Materials and Devices, Key Laboratory of Specially Functional Materials, South China University of Technology, Guangzhou 510640, P. R. China.

E-mail: poycao@scut.edu.cn; psjbpeng@scut.edu.cn;

Fax: +(86) 20 8711 0606; Tel: +(86) 20 8711 4609

[†] Electronic supplementary information (ESI) available: NMR, CV and DSC data. See DOI: 10.1039/b609250k

[‡] The HTML version of this article has been enhanced with colour images.

1.1 cd A^{-1} .^{12*a*} Hung *et al.* reported TAZ-end-capped polylfluorenes showing blue emission peaked at 442 nm with a maximum efficiency of 1.67 cd A^{-1} and CIE coordinates of (0.165, 0.076).^{8*c*}

In our previous work, we synthesized poly(3,6-silafluorene) (PSiF) homopolymers via the Yamamoto coupling reaction,¹³ Similar polymers were soon after reported via a different synthetic route.¹⁴ Unlike poly(2,7-silafluorene),¹⁵ poly(3,6silafluorene) homopolymers showed an extremely wide bandgap (ca. 4 eV) with a PL emission peak in the violet region (360–370 nm).¹³ As was reported by Chan et al.,¹⁵ both the poly(2,7-silafluorene) homopolymer and the poly(2,7-silafluorene-alt-2,7-fluorene) copolymer showed EL and PL properties similar to those of poly(9,9-dioctyl-2,7-fluorene) (PFO). It will be interesting to see how the incorporation of a wide bandgap 3,6-silafluorene unit into the polyfluorene main chain would affect the emitting properties of the copolymers. In this paper, we report the synthesis and characterization of a new series of copolymers (PSiFF) based on 3,6-silafluorene (SiF) and 2,7-fluorene. The influences of the 3,6-silafluorene content in the copolymers on the thermal, photophysical, EL and electrochemical properties were investigated. Both fluorene and 3.6-silafluorene are expected to take part in π -conjugation of the main chain and thereby the emission spectra will be significantly blue-shifted with increasing the wide bandgap 3,6silafluorene content. We found out that the incorporation of 3,6-silafluorene into the polyfluorene main chain suppresses the long-wavelength emission and improves the spectral stability of the copolymers at annealing and the device efficiencies.

Experimental

Materials

All chemicals and reagents were used as received from Aldrich, ABCR, and Acros Chemical Co. unless otherwise specified. All solvents were carefully dried and purified under nitrogen. All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere.

Measurement and characterization

¹H and ¹³C NMR spectra were recorded on a Bruker AV-300 (300 MHz and 75 MHz respectively) in deuterated chloroform or dimethyl sulfoxide solution. The Fourier transform infrared (FTIR) spectra of all complexes were recorded on a Bruker FTIR spectrometer using KBr pellets at room temperature. Melting points were determined using a polarized optical microscope of Zeiss Axiophot with a Linkam hot stage. GC-MS experiments were recorded on a Finnigan Trace 2000. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve with standard polystyrene as a reference. The elemental analyses were performed on a Vario EL elemental analysis instrument (ELEMENTAR Co.). UV-vis absorption spectra were recorded on a Hitachi UV-3010 spectrophotometer. The PL quantum yields were determined in an integrating sphere IS080 (Labsphere) with 325 nm excitation of a HeCd laser (Mells Griot).

Synthesis

2,7-Dibromo-9,9-dioctylfluorene (8) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (9) were prepared according to the published procedures.¹⁶

N,N'-Biphenyl-2,2'-divlbiacetamide (3). When a mixture of 2,2'-dinitrobiphenyl (1) (20.0 g, 82.0 mmol), iron powder (40.0 g, 714 mmol) and ethanol (1000 mL) was heated to reflux, aqueous HCl (36% w/w, 120 mL) was added dropwise over 30 min. After refluxing for a further 2 h, the excess iron powder was filtered off and the filtrate was evaporated to dryness. The residue was added to a mixture of citric acid (110.0 g, 0.52 mol) and potassium sodium tartrate (130.0 g, 0.46 mol) in 500 mL of water. Then saturated aqueous Na₂CO₃ solution was added until the pH reached 8. The precipitate was filtered and then washed with water to give 2,2'-diaminobiphenyl (2), which was added to a Na₂CO₃ solution (30 g in 200 mL of water) with acetic anhydride (50 mL). After being cooled to 0 °C, 3 was obtained by filtration. Recrystallization from ethanol-water (3:1) afforded 3 as white crystals (13.0 g, 59%). Mp 168-169 °C. GC-MS (EI m/z): 268 (M⁺). Anal. Calcd for C₁₆H₁₆N₂O₂ (%): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.58; H, 6.69; N, 10.70. IR (solid state): 3291, 3206, 3173, 3013, 2821, 1660, 1578, 1532, 1470, 1450, 1433, 1369, 1312, 1298, 1032, 1007, 972, 944, 768, 746 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ(ppm) 8.07 (2H, d, J = 8.1, ArH), 7.42 (2H, t, J = 9.1, ArH), 7.24 (4H, m, ArH), 7.06 (2H, b, NH), 1.96 (6H, s, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ(ppm) 169.2, 135.4, 130.5, 129.3, 125.3, 123.6, 77.1, 24.1.

N,*N*'-(**5**,**5**'-Dibromobiphenyl-2,2'-diyl)biacetamide (4). A mixture of **3** (10.0 g, 37.3 mmol), *N*-bromosuccinimide (14.2 g, 79.8 mmol) and *N*,*N*-dimethylformamide (100 mL) was stirred for 12 h at room temperature, and then poured into 200 mL of water. The precipitate was filtered and washed with water. Recrystallization from ethanol afforded **4** as a yellow–white powder (14.0 g, 88%). Mp 280 °C. Anal. Calcd for C₁₆H₁₄Br₂N₂O₂ (%): C, 45.10; H, 3.31; N, 6.57. Found: C, 44.93; H, 3.51; N, 6.67. IR (solid state): 3356, 3057, 2931, 1675, 1575, 1515, 1450, 1413, 1392, 1374, 1298, 1085, 1025, 888, 828, 695, 664, 597 cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ (ppm) 8.92 (2H, d, *J* = 11.6, N*H*), 7.56 (4H, b, A*rH*), 7.39 (2H, t, A*rH*), 1.80 (6H, d, *J* = 2.8, CH₃). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm) 169.1, 135.6, 133.7, 133.6, 131.5, 127.8, 117.5, 23.5.

5,5'-Dibromo-2,2'-diiodobiphenyl (6). To a refluxing solution of **4** (10.0 g, 23.5 mmol) in ethanol (200 mL) and water (200 mL) was added dropwise concentrated HCl (100 mL). After refluxing for a further 3 h, the ethanol was evaporated off. NaOH was added to the mixture until the pH reached 10. The precipitate was filtered to yield 5,5'-dibromobiphenyl-2,2'-diamine (**5**), which was added to a mixture of sodium nitrite (3.4 g, 49.3 mmol in 30 mL of water) and HCl (w/w 36%, 24 mL in 50 mL water) at 0 °C in 10 min. After stirring for a further 20 min, the mixture was added within 30 min to a vigorously stirred solution of KI (83.0 g, 0.5 mol) in 200 mL of water at room temperature, and then stirred overnight. NaOH

solution was added until the pH reached 7. The solution was extracted several times with diethyl ether. The organic layer was washed with water, dried over anhydrous MgSO₄, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent to yield **6** as an off-white solid (4.3 g, 32%). Mp 207–210 °C. GC-MS (EI *m/z*): 564 (M⁺). Anal. Calcd for C₁₂H₆Br₂I₂ (%): C, 25.56; H, 1.07. Found: C, 25.77; H, 0.77. IR (solid state): 3072, 3054, 2920, 2850, 1629, 1562, 1535, 1437, 1385, 1354, 1086, 1058, 1040, 1016, 998, 879, 822, 806, 722, 710, 698, 665, 624, 455 cm^{-1. 1}H NMR (300 MHz, CDCl₃) *δ*(ppm) 7.80 (2H, d, *J* = 8.4, Ar*H*), 7.34 (2H, d, *J* = 2.3, Ar*H*), 7.24 (2H, dd, *J* = 8.5, 2.4, Ar*H*). ¹³C NMR (75 MHz, CDCl₃) *δ*(ppm) 149.3, 140.3, 132.9, 132.6, 122.3, 97.3.

3.6-Dibromo-9.9-di-n-octvlsilafluorene (7). To a solution of 6 (3 g, 5.32 mmol) in THF (50 mL) at -100 °C was added dropwise 1.6 mol L^{-1} *n*-BuLi in hexane (11.6 mL, 18.6 mmol) over 1 h. The resulting mixture was stirred for a further 2 h at -100 °C. After that, di-n-octyldichlorosilane (3.44 g, 10.6 mmol) was added and the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with distilled water, and then the product was extracted with diethyl ether. The organic layer was washed with brine and water, dried over anhydrous MgSO4 and evaporated. The residue was chromatographed on silica gel using hexane as the eluent to yield 7 as a colorless oil (2.1 g, 70%). GC-MS (EI m/z): 564 (M⁺). Anal. Calcd for C₂₈H₄₀Br₂Si (%): C, 59.57; H, 7.14. Found: C, 59.67; H, 7.18. IR (solid state): 3066, 3037, 2956, 2923, 2854, 2670, 1626, 1578, 1538, 1457, 1393, 1373, 1260, 1244, 1086, 1063, 1013, 871, 819, 752, 726, 529, 416 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.91 (2H, d, J = 1.4, Ar*H*), 7.46 (2H, d, J = 7.6, ArH), 7.42 (2H, dd, J = 7.6, 1.5, ArH), 1.19–1.28 (24H, m, CH_2), 0.91 (4H, m, CH_2), 0.87 (6H, t, J = 7.1, CH_3), ¹³C NMR (75 MHz, CDCl₃) δ(ppm) 149.1, 136.8, 134.5, 130.6, 125.2, 124.7, 33.2, 31.8, 29.3, 29.1, 29.0, 23.8, 22.6, 14.3.

General procedure of polymerization¹⁵. Carefully purified monomer 7, 8, 9, tricyclohexylphosphine (5–7 mol%), and palladium(II) acetate (1.5–2 mol%) were dissolved in a mixture of toluene ([monomer] = 0.1 mol L^{-1}) and aqueous tetraethylammonium hydroxide (20% w/w, 3:2 in volume) under argon. The resulting mixture was refluxed by vigorously stirring for 48 h, and then cooled to room temperature and poured into methanol. The precipitated material was collected by filtration through a funnel. The polymer was purified by washing with acetone for 24 h to remove catalyst residues.

Copolymer PSiFF50. Monomer **7** (0.50 equiv.) and monomer **9** (0.50 equiv.) were used in this polymerization. Anal. Calcd for polymer (%): C, 86.30; H, 10.16. Found: C, 85.83; H, 10.31. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.44–7.84 (brm, Ar*H*), 2.07 (b, C*H*₂), 0.68–1.46 (brm, C*H*₂+C*H*₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 151.8, 149.1, 144.7, 142.1, 140.4, 135.4, 135.0, 128.6, 128.0, 126.1, 121.44, 120.1, 55.4, 40.5, 33.5, 31.9, 31.7, 30.0, 29.7, 29.3, 29.2, 24.9, 24.1, 23.8, 23.2, 23.0, 22.7, 22.6, 16.5, 14.1, 12.5. Other copolymers showed similar ¹H NMR spectra to that of PSiFF50.

Copolymer PSiFF70. Monomer **7** (0.30 equiv.), monomer **8** (0.20 equiv.), and monomer **9** (0.50 equiv.) were used in this polymerization. Anal. Calcd for polymer (%): C, 87.61; H, 10.25. Found: C, 86.34; H, 10.36.

Copolymer PSiFF90. Monomer **7** (0.10 equiv.), monomer **8** (0.40 equiv.), and monomer **9** (0.50 equiv.) were used in this polymerization. Anal. Calcd for polymer (%): C, 88.95; H, 10.33. Found: C, 88.54; H, 10.32.

Copolymer PSiFF95. Monomer 7 (0.05 equiv.), monomer 8 (0.45 equiv.), and monomer 9 (0.50 equiv.) were used in this polymerization. Anal. Calcd for polymer (%): C, 89.29; H, 10.35. Found: C, 88.73; H, 10.41.

Device fabrication and characterization

The LED was fabricated on prepatterned indium-tin oxide (ITO) with a sheet resistance of 10-20 ohm square⁻¹. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol subsequently. Onto the ITO glass a layer of polyethylenedioxythiophene-polystyrene sulfonic acid (PEDOT : PSS) film with a thickness of 40 nm was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG). The PEDOT-PSS film was dried at 80 °C for 8 h in a vacuum oven. Then polyvinylcarbazole (PVK) was spincoated onto PEDOT-PSS and dried at 80 °C for 2 h under nitrogen. The solution of the copolymers in toluene was spincoated onto the ITO/PEDOT : PSS/PVK surface. After that, a thin layer of barium as an electron injection cathode and the subsequent 150 nm thick aluminium capping layer were thermally deposited by vacuum evaporation through a mask at a base pressure below 2 \times 10⁻⁴ Pa. The deposition speed and thickness of the barium and aluminium layers were monitored by a thickness/rate meter (model STM-100, Sycon Instrument, Inc.). The spin coating of the EL layer and the device performance tests were carried out within a glove box (Vacuum Atmosphere Co.) with nitrogen circulation. Current-voltage (I-V) characteristics were measured with a computerized Keithley 236 Source Measure Unit. The luminance of the device was measured with a photodiode calibrated by using a PR-705 SpectraScan Spectrophotometer (Photo Research). External quantum efficiency was verified by measurement in the integrating sphere (IS080, Labsphere) after encapsulation of the devices with UV-cured epoxy and thin cover glass.

Results and discussion

Synthesis and characterization

The chemical structures and synthetic routes of 3,6-(9,9-din-octylsilafluorene) monomer and copolymers are outlined in Schemes 1 and 2. 1 was reduced with iron powder to the corresponding diamine 2. Acetic anhydride added to the mixture of 2 without further purification in Na₂CO₃ aqueous solution gave stable 3 in 59% yield. The bromination of 3 took place selectively at the 5,5'-position to give 4 in 88% yield. The 5 obtained by hydrolysis of 4 was diazotized with sodium nitrite in dilute hydrochloric acid to give 6 in a low yield (32%)



Scheme 1 Synthesis of 3,6-dibromo-9,9-di-n-octylsilafluorene.

owing to the formation of a byproduct dibenzoiodonium iodide salt.^{15,17} n-BuLi was added dropwise to the THF solution of 6 followed by addition of di-n-octyldichlorosilane to afford 7 in 70% yield.¹⁸ The PSiFF copolymers based on monomers 7, 8 and 9^{16} were synthesized *via* a modified Suzuki polycondensation (Scheme 2).¹⁵ In order to obtain high molecular weights, the monomers were purified carefully by column chromatography on silica gel and their purities were determined by elemental analysis and NMR before use. The feed compositions of monomer 7 in the polycondensation were 50, 30, 10, and 5 mol%, and the corresponding copolymers are respectively named PSiFF50, PSiFF70, PSiFF90, and PSiFF95. The copolymers are readily soluble in common organic solvents, such as toluene, xylene, THF and chloroform. The chemical structures of the polymers were verified by ¹H NMR, ¹³C NMR, and elemental analyses. The number-average molecular weights $(M_{\rm p})$ of the polymers determined by gel permeation chromatography (GPC) ranged from 19000 to 39000 with polydispersity indices of 1.4 to 2.5 using polystyrene as the standard. To investigate the thermal stability of the copolymers, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed. All the copolymers exhibited good thermal stability with degradation temperatures (T_d) of 395–418 °C (5% weight loss). DSC results indicate that T_g is very sensitive to the content of 3,6-silafluorene unit. As we reported previously, the poly(3,6-silafluorene) homopolymer showed much lower T_{g}



Scheme 2 Synthesis of copolymers.

than the corresponding PFO homopolymer (see Table 1), so it would be expected that incorporation of the SiF unit into the PFO backbone would lead to lower T_g for the copolymer. Surprisingly, with an initial increase of SiF molar ratio in the copolymers, T_g increases to 80 °C for PSiFF90 and then decreases with further increase in SiF molar ratio, reaching the level of the PSiF homopolymer for PSiFF50. As we will show below PSiFF90 gives the best device performance and the narrowest EL emission peak. At this stage of experiment, it is not clear why T_g increases with the initial incorporation of SiF unit in the copolymers. Further morphological and structural studies are in progress and the results will be reported in a forthcoming paper. The molecular weights and thermal data of the polymers are summarized in Table 1.

Electrochemical properties

The electrochemical behaviors of the polymers were investigated by cyclic voltammetry (CV); the results are summarized in Table 2. CV was performed on a Potentiostat Galvanostat Model 283 (Princeton Applied Research) electrochemical workstation with platinum working electrodes at a scan rate of 50 mV s⁻¹ against a calomel reference electrode with a nitrogen-saturated anhydrous solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN). The evaporation-deposition of polymers onto the working electrode was conducted from a dilute chloroform solution. All the polymers displayed reversible p-doping and the onset potentials for oxidation were 1.55, 1.44, 1.40, 1.38, and 1.40 V for PSiFF50, PSiFF70, PSiFF90, PSiFF95, and PFO, respectively. However, the reduction

 Table 1
 Molecular weights and thermal data of the polymers

Polymers	Yield (%)	$M_{\rm n} \; (\times 10^4)$	$M_{\rm w} (\times10^4)$	$M_{\rm w}/M_{\rm n}$	$T_{\rm d}/^{\circ}{\rm C}$	$T_{\rm g}/^{\circ}{\rm C}$
PSiF ^a	_	1.0	1.6	1.6	442	58
PSiFF50	50	1.9	2.6	1.39	395	58
PSiFF70	60	2.4	5.5	2.25	418	60
PSiFF90	80	3.2	8.0	2.49	408	80
PSiFF95	85	3.9	9.4	2.41	408	72
PFO	85	4.5	10.1	2.24	385	72
^a Data of	poly(3,6	5-(9,9-dihexyl)	silafluorene)	taken fron	n referer	ice 13.

Polymer	HOMO/eV	LUMO/eV	E_{g}/eV	Solution in THF λ_{max}/nm		Film $\lambda_{\rm max}/{\rm nm}$			
				Abs	PL	Abs	PL	FWHM	$\phi_{ m PL}$
PSiF ^a	-6.1	-2.1	4.0	283	365	283	363	46	14%
PSiFF50	-5.95	-2.62	3.33	333	376, 414	332	398, 418	59	38%
PSiFF70	-5.84	-2.87	2.97	356	415, 436	357	418, 442	47	77%
PSiFF90	-5.80	-2.86	2.94	384	415, 439	378	422, 443	46	84%
PSiFF95	-5.78	-2.86	2.92	386	416, 438	380	422, 445	46	71%
PFO	-5.80	-2.87	2.93	384	416, 438	381	431, 446	48	67%
^a Data of p	oly(3,6-(9,9-dihex)	yl)silafluorene) ta	ken from ret	ference 13.					

Table 2 Electrochemical and optical properties of the polymers

processes were hardly recorded after many attempts. The HOMO levels of the polymers were calculated according to the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.40) \text{ (eV)},^{19}$ the LUMO levels of the copolymers estimated by subtraction of the optical bandgap E_{g} (eV) from the HOMO values.

Optical and photoluminescence properties

The absorption spectra of the polymers in THF solution and films spin-coated from toluene solution are shown in Fig. 1a and b, respectively. The absorption spectra of the polymers in the solid state are similar to (a little broader than) those of the corresponding copolymers in THF solution. The optical bandgaps deduced from the absorption edge and the optical properties are summarized in Table 2. The absorption spectra of the poly(3,6-silafluorene) homopolymers synthesized in our previous work¹³ are also included in Fig. 1 for comparison. As we reported previously, poly(3,6-silafluorene) had a very wide bandgap and showed the absorption maximum at 283 nm,¹³ while that of PFO homopolymer was observed at 381 nm. Unlike most polyfluorene-based copolymers containing narrow bandgap units showing two distinguished absorption



Fig. 1 UV-vis spectra of the polymers: (a) in THF solution and (b) in the solid state.

peaks responsible for wide and narrow bandgap units, the relative intensities of which change with the relative ratios of the comonomer composition in the copolymers,²⁰ poly(3,6silafluorene-co-2,7-fluorene) showed only one absorption peak blue-shifting from 381 nm (for neat PFO) to 283 nm (for neat PSiF) with increasing 3,6-silafluorene content in the copolymers (Fig. 1b). There are two possible mechanisms for the significant blue shift in the copolymers. One is that the blue shift might originate from both fluorene and 3,6-silafluorene comonomers taking part in the π -conjugation along the polymer backbone and forming a uniform band structure by mixing the electronic states of the two monomer units.²¹ As reported previously,¹³ the poly(3,6-silafluorene) homopolymer has a wider bandgap than PFO. As a result, the bandgaps of the copolymers increase with increasing 3,6-silafluorene content. The other is that the blue shift might result from the interruption of the delocalization of the π -electrons along the polymer backbone by the isolated 3,6-silafluorene linkages. In this case, the 3,6-silafluorene unit does not join in the π -conjugation but functions only as a defect which breaks the π -conjugation of the PFO main chain.²² However, judging from the absorption peaks of the fluorene oligomers²³ and the PSiFF copolymers, the latter mechanism is less probable, for the peak position of the PSiFF copolymers with statistically distributed PFO units: 50/50 (corresponding an isolated monomer unit): 332 nm; 70/30 (corresponding to statistically 2.3 units): 357 nm is much more bathochromic than that of the corresponding fluorene oligomers: 329 nm for the dimer, 349 nm for the trimer and 363 nm for the tetramer.²³

The PL spectra of the polymers in THF solution and in films are shown in Fig. 2a and b, respectively. Except for PSiFF50, the PL spectra of the other copolymers in films were only slightly red shifted with respect to their corresponding spectra in solution, indicating that there were no noticeable molecular conformation changes from solution to the solid state. As shown in Fig. 2b the PL spectra of the PSiFF copolymers in films show lower intensity of the shoulder at 460-490 nm compared to those of the polyfluorene homopolymer (PFO) which demonstrates that the incorporation of 3,6-silafluorene could effectively suppress the π -stacking/aggregation of polyfluorenes in the solid state. As a result, the color purity of the copolymer-based devices is significantly improved. Similar to the absorption spectra, the PL spectra of the PSiFF copolymers in films are significantly blue-shifted from 431 nm for the PFO homopolymer to 420, 416 and 400 nm for PSiFF90, PSiFF70 and PSiFF50 respectively with increasing 3,6-silafluorene content in the copolymers. All the PSiFF



Fig. 2 PL spectra of the polymers: (a) in THF solution $(10^{-5} \text{ mol } \text{L}^{-1})$ and (b) in the solid state.

copolymers show similar PL profiles in solid state except the alternating copolymer PSiFF50. Absolute PL efficiencies of the copolymer films measured in the integrating sphere increase initially reach the maximum of 84% for PSiFF90 with increasing 3,6-silafluorene content, and then decrease very quickly to 38% for the alternating copolymer PSiFF50 with further increase in 3,6-silafluorene content (Table 2). The fact that the PL emission profile for PSiFF50 is much broader than those of the other copolymers (Fig. 2b) is consistent with the fact of the reduced PL efficiency for the alternating copolymer PSiFF50.

Electroluminescence properties

To investigate the EL properties of the copolymers, doublelayer devices were fabricated with a configuration of ITO/ PEDOT : PSS(40 nm)/PVK(40 nm)/polymer(80 nm)/Ba(4 nm)/ Al(150 nm), in which PEDOT–PSS and PVK respectively represent poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) and polyvinylcarbazole as hole injection/transport layers. Fig. 3 shows the EL spectra of the devices from the copolymers. The peak position of EL emission of the copolymers was close to that of the PL emission (Fig. 2b). In contrast with the distinct fine vibronic structure of the PL emission in the solid state, the relative intensity of the vibronic shoulders of the EL



Fig. 3 EL spectra of the devices fabricated from the PSiFF copolymers.

emission decreased with increasing 3,6-silafluorene content except for the alternating copolymer, which showed a broadening of both the EL peak and the PL peak. As a result, the full widths at half maximum (FWHM) of the EL spectra for PSiFF90 (19 nm) and PSiFF70 (15 nm) (Table 3) decreased dramatically in comparison with those of the PL spectra for the corresponding copolymers in the solid state. Band narrowing is very important for the improvement of the color purity of polymer LEDs, for the FWHM of π -conjugated emitting polymers are typically more than 50 nm due to the broad distribution of the conjugation length and the formation of interchain emissive species.²⁴ Following Ariu et al.²⁵ the decrease in the intensity of the lower energy vibronic emissive states with increasing 3,6-silafluorene content in the copolymers suggests that the chain rigidity of the PSiFF copolymers has been significantly enhanced due to the incorporation of 3,6-silafluorene into the polyfluorene main chain. Similarly, that EL emission peaks are narrower than their PL emission peaks has been reported for oligoarylfluorenes bearing oligothiophene as a central core by the Tao group,²⁶ which is attributed to the different contributions of vibronic states in the EL and PL processes.²⁶ Further experiments are in progress to get a full understanding of the origin behind the phenomenon. As a result of band narrowing, the CIE coordinates (0.18, 0.09), (0.18, 0.15), and (0.16, 0.07) have been reached (Fig. 4) for PSiFF50, PSiFF70, and PSiFF90, respectively. These values are among the CIE coordinates of the best deep-blue polymer emitters. It is important to note that not only does the incorporation of 3,6-silafluorene into the polyfluorene main chain efficiently suppress the longwavelength emission (compared to the EL emission of the PFO homopolymer in Fig. 3), the spectral stability after high temperature annealing is also significantly improved. Fig. 5 compares the changes of the EL spectra of PSiFF90 and PFO homopolymer after annealing for 1 h at 150 °C under nitrogen. In contrast to the pronounced increase in the long-wavelength

Table 3 EL performance of the polymers in devices with the configuration of ITO/PEDOT/PVK/polymer/Ba/Al at 20 mA cm⁻²

Polymer	$\lambda_{\rm EL,max}/\rm nm$	FWHM/nm	CIE 1931	LE/cd A ⁻¹	EQE (%)	$L/cd m^{-2}$	Voltage/V
PSiFF50	400	57	0.18, 0.09	0.96	0.75	189	11.2
PSiFF70	416	15	0.18, 0.15	0.43	1.36	96	10.1
PSiFF90	420	19	0.16, 0.07	2.02	3.34	326	6.7
PSiFF95	418	53	0.16, 0.12	0.47	1.42	90	8.3
PFO	438	35	0.19, 0.19	0.36	0.51	66	10.3



Fig. 4 CIE coordinates of the devices fabricated from the PSiFF copolymers.

emission for the PFO homopolymer, almost no change was observed for PSiFF90 after annealing. The improved thermal stability of the EL emission may be related partially to the higher T_g of PSiFF90 copolymer. It is reported that the higher color purity of electroluminescence devices based on conjugated oligomers is usually associated with their higher glass transition temperatures.²⁷ We note that Chan *et al.* also reported that poly(2,7-dibenzosilole) showed significantly improved color purity after thermal annealing over polyfluorenes.¹⁵

The EL performance of the polymers at 20 mA cm⁻² is summarized in Table 3. Of all the copolymers, the device from the PSiFF90 copolymer showed the best performance with an external quantum efficiency of 3.34% and a luminous efficiency of 2.02 cd A⁻¹ at a luminance of 326 cd m⁻². Luminous efficiency–current density–luminance (LE–*J*–*L*) and current density–voltage–luminance (*J*–*V*–*L*) characteristics of the PSiFF90-based device are plotted in Fig. 6 and 7, respectively. As shown in Fig. 6, the device efficiency remains as high as 1.1 cd A⁻¹ at a current density of 500 mA cm⁻² with the luminance over 5000 cd m⁻². The results indicate poly(3,6silafluorene-co-2,7-fluorene) could be a promising candidate for blue-emitting polymers of high efficiency and good color purity.

Conclusions

In conclusion, 3,6-silafluorene was successfully incorporated into the polyfluorene main chain. The incorporation of the



Fig. 5 EL spectra of PSiFF90 and PFO before and after annealing at 150 °C for 1 h under nitrogen.



Fig. 6 LE–J–L characteristics of the device based on PSiFF90.



Fig. 7 J-V-L characteristics of the device based on PSiFF90.

3,6-silafluorene unit not only suppressed the long-wavelength emission but the efficiency and color purity of PSiFF copolymer-based devices are significantly improved. The device based on copolymer PSiFF90 exhibited high performance with an external quantum efficiency of 3.34% and a luminous efficiency of 2.02 cd A^{-1} at a brightness of 326 cd m^{-2} with a surprisingly narrow FWHM (19 nm) and CIE coordinates of (0.16, 0.07), which almost match the NTSC standard blue pixel coordinates of (0.14, 0.08) (see Fig. 4). The results are among the best reported for pure blue-emitting polymers in the literature so far. Moreover, the incorporation of 3,6-silafluorene into the polyfluorene main chain significantly enhances the spectral stability of copolymers at annealing. The fascinating properties of poly(3,6-silafluoreneco-2,7-fluorene) copolymers show that the incorporation of a wide bandgap 3,6-silafluorene into the π -conjugated polyfluorenesmain chain is a promising route to high-efficiency spectrum-stable color-pure blue-emitting polymers.

Acknowledgements

This work was supported by research grants from the Ministry of Science and Technology, China (MOST) Project (#2002CB613402) and the National Science Foundation of China (NSFC) Project (#50433030).

References

- (a) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539; (b) D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
- 2 (a) C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker and

K. Meerholz, *Nature*, 2003, **421**, 829; (*b*) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.

- 3 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
- 4 (a) M. Leclerc, J. Polym. Sci., Part A: Polym. Chem., 2001, 39, 2867; (b) D. Neher, Macromol. Rapid Commun., 2001, 22, 1365; (c) U. Scherf and E. J. W. List, Adv. Mater., 2002, 14, 477.
- 5 (a) V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klärner, R. D. Miller and D. C. Miller, *Macromolecules*, 1999, **32**, 361; (b) D. Marsitzky, J. C. Scott, J. P. Chen, V. Y. Lee, R. D. Miller, S. Setayesh and K. Müllen, *Adv. Mater.*, 2001, **13**, 1096; (c) K. H. Weinfurtner, H. Fujikawa, S. Tokito and Y. Taga, *Appl. Phys. Lett.*, 2000, **76**, 2502; (d) C. Ego, A. C. Grimsdale, F. Uckert, G. Yu, G. Srdanov and K. Müllen, *Adv. Mater.*, 2002, **14**, 809.
- 6 (a) E. J. W. List, R. Guentner, P. S. Freitas and U. Scherf, Adv. Mater., 2002, 14, 374; (b) X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger and S. S. Xiao, Adv. Funct. Mater., 2003, 13, 325.
- 7 (a) L. Romaner, A. Pogantsch, P. S. de Freitas, U. Scherf, M. Gaal,
 E. Zojer and E. J. W. List, *Adv. Funct. Mater.*, 2003, 13, 597; (b)
 M. Gaal, E. J. W. List and U. Scherf, *Macromolecules*, 2003, 36, 4236.
- 8 (a) S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E. J. W. List and G. Leising, *J. Am. Chem. Soc.*, 2001, **123**, 946; (b) W. Yang, Q. Hou, C. Z. Liu, Y. H. Niu, J. Huang, R. Q. Yang and Y. Cao, *J. Mater. Chem.*, 2003, **13**, 1351; (c) M. C. Hung, J. L. Liao, S. A. Chen, S. H. Chen and A. C. Su, *J. Am. Chem. Soc.*, 2005, **127**, 14576.
- 9 H. J. Su, F. I. Wu, Y. H. Tseng and C. F. Shu, Adv. Funct. Mater., 2005, 15, 1209.
- 10 W. S. Wu, M. Inbasekaran, M. Hudack, D. Welsh, W. L. Yu, Y. Cheng, C. Wang, S. Kram, M. Tacey, M. Bernius, R. Fletcher, K. Kiszka, S. Munger and J. O'Brien, *Microelectron. J.*, 2004, 35, 343.
- 11 T. Jüstel, H. Nikol and C. Ronda, Angew. Chem., Int. Ed., 1998, 37, 3084.
- 12 (a) T. Miteva, A. Meisel, W. Knoll, H. G. Nothofer, U. Scherf, D. C. Müller, K. Meerholz, A. Yasuda and D. Neher, *Adv. Mater.*, 2001, **13**, 565; (b) J. P. Chen, G. Klaerner, J. I. Lee, D. Markiewicz,

V. Y. Lee, R. D. Miller and J. C. Scott, *Synth. Met.*, 1999, **107**, 129; (c) Y. H. Tseng, P. I. Shih, C. H. Chien, A. K. Dixit, C. F. Shu, Y. H. Liu and G. H. Lee, *Macromolecules*, 2005, **38**, 10055.

- 13 Y. Q. Mo, R. Y. Tian, W. Shi and Y. Cao, *Chem. Commun.*, 2005, 4925.
- 14 K. L. Chan, S. E. Watkins, C. S. K. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascu and A. B. Holmes, *Chem. Commun.*, 2005, 5766.
- 15 K. L. Chan, M. J. McKiernan, C. R. Towns and A. B. Holmes, J. Am. Chem. Soc., 2005, 127, 7662.
- 16 (a) Q. Hou, Y. S. Xu, W. Yang, M. Yuan, J. B. Peng and Y. Cao, J. Mater. Chem., 2002, **12**, 2887; (b) R. Q. Yang, R. Y. Tian, W. Yang, Q. Hou and Y. Cao, Macromolecules, 2003, **36**, 7453; (c) M. Ranger, D. Rondeau and M. Leclerc, Macromolecules, 1997, **30**, 7686.
- 17 W. C. Lothrop, J. Am. Chem. Soc., 1941, 63, 1187.
- 18 Y. X. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei and R. West, J. Am. Chem. Soc., 2002, 124, 49.
- 19 D. M. Leeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand, Synth. Met., 1997, 87, 53.
- 20 (a) Q. Hou, Q. M. Zhou, Y. Zhang, W. Yang, R. Q. Yang and Y. Cao, *Macromolecules*, 2004, **37**, 6299; (b) R. Q. Yang, R. Y. Tian, J. A. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang and Y. Cao, *Macromolecules*, 2004, **38**, 244.
- 21 G. Klärner, M. H. Davey, W. D. Chen, J. C. Scott and R. D. Miller, *Adv. Mater.*, 1998, **10**, 993.
- 22 M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott and R. D. Miller, *Macromolecules*, 1998, **31**, 1099.
- 23 J. Jo, C. Chi, S. Hoger, G. Wegner and D. Y. Yoon, *Chem. Eur. J.*, 2004, **10**, 2681.
- 24 (a) Y. Zhang, J. B. Peng, Y. Q. Mo and Y. Cao, *Appl. Phys. Lett.*, 2004, **85**, 5170; (b) M. T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.
- 25 M. Ariu, M. Sims, M. D. Rahn, J. Hill, A. M. Fox, D. G. Lidzey, M. Oda, J. Cabanillas-Gonzalez and D. D. C. Bradley, *Phys. Rev. B*, 2003, **67**, 195333.
- 26 Z. H. Li, M. S. Wong, H. Fukutani and Y. Tao, *Chem. Mater.*, 2005, **17**, 5032.
- 27 J. Salbeck, N. Yu, J. Bauer, F. Weissörtel and H. Bestgen, *Synth. Met.*, 1997, **91**, 209.