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Electroluminescence performances of 1,1-bis(4-(*N*,*N*-dimethylamino)phenyl)-2,3,4,5-tetraphenylsilole based polymers in three cathode architectures[†]

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A new silole monomer with two 4-(*N*,*N*-dimethylamino)phenyl substitutions on silicon atom as designed and synthesized. Three copolymers PF-N-HPS1, PF-N-HPS10 and PF-N-HPS20 were then obtained by copolymerizations of 2,7-fluorene derivatives with the silole monomer at feed ratios of 1%, 10%, and 20%. Their UV-vis absorption, electrochemical, photoluminescent, and electroluminescent (EL) properties were investigated. PF-N-HPS possessed HOMO levels of -5.25--5.58 eV, and showed green emissions. Using PF-N-HPS as the emissive layer, three different polymer light-emitting diodes were fabricated as device A with ITO/PEDOT/PF-N-HPS/Al, device B with ITO/PEDOT/PF-N-HPS/Ba/Al, and device C with ITO/PEDOT/PF-N-HPS/TPBI/Ba/Al. For the device A, PF-N-HPS only showed very low EL efficiency of 0.06–0.33 cd/A, indicating that the Al cathode could not inject electron efficiently to the emissive polymers containing the 4-(*N*,*N*-dimethylamino)phenyl groups. For the device B, low work function Ba supplied better electron injections, and the EL efficiency could be improved to 0.85–1.44 cd/A. TPBI with a deep HOMO level of -6.2 eV could enhance electron transport and hole blocking. Thus modified recombinations and largely elevated EL efficiency of 4.56–7.96 cd/A were achieved for the device C. The separation of the emissive layer may also suppress exciton quenching at the cathode interface.

silole-containing polymers, N,N-dimethylaminobenzene, polyfluorene, electroluminescence

1 Introduction

Siloles or silacyclopentadienes [1] are a group of fivemembered heterocycles, with structural characterization of $\sigma^*-\pi^*$ conjugation arising from the σ^* orbital of two σ^* bonds on the silicon atom and the π^* orbital of the butadiene moiety. Such $\sigma^*-\pi^*$ interaction usually has lower LUMO levels than other five-membered systems such as pyrroles, furans an thiophenes [2]. Fully substituted siloles, i.e, with two groups on the silicon atom and four groups on the ring carbons of the butadiene, can be realized, meanwhile large fused-rings containing a silole core, e.g., dibenzosilole and dithienosilole, can be formed. Some siloles possess outstanding optoelectronic properties, as high electron affinity and fast electron mobility were observed for those fused with electron-deficient aromatic rings [3]. A series of 2,3,4,5-tetraphenylsiloles with different 1,1disubstitutions displayed novel aggregation-induced emission (AIE) [4–6], giving high PL quantum yields (Φ_{PL}) up to 100% in an amorphous form and 80% in a crystalline form [7, 8]. In addition, the organic light-emitting diodes (OLEDs) [9, 10] could generate very high electroluminescent (EL) efficiency, for example, an external quantum efficiency (η_{EL}) of 8% was realized when 1-methyl-

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1,2,3,4,5-pentaphenylsilole was used as emissive layer, and an η_{EL} of 7% was reported for 1,1,2,3,4,5- hexaphenylsilole (HPS) [11]. Considerable interest has been attracted to silole-containing polymers due to their unique optoelectronic properties [12]. High Φ_{PL} of >80% and η_{EL} of ~3% have been achieved for the polymer light-emitting diodes (PLEDs) with silole-containing polymers as the emissive layer [13, 14]. Another example is the application of dithienosilole-based polymers, which gave high hole mobility of an order of 10^{-2} cm²/Vs in field effect transistors and energy conversion efficiency over 7% in polymer solar cells (PSC) [15–17]. Moreover, dibenzosilole-based polymers showed good luminescent and photovoltaic properties [18].

The polymers with 2,5-difunctionalized siloles produced interesting emissions, and the band gap could be tuned through different 2,5-difunctionalizations. For example, green emissions were observed for the polymers with 2,5-diphenylsilole [13] and 2,5-difluorenylsilole [19] as the building blocks, while red emissions were reported for the 2,5-dithienylsilole-based polymers [20]. Other silole monomers with 3,4- [21] or 1,1-difunctional groups were also synthesized. However, the 1,1-difunctionalized silole monomers are very limited, only involving 1-methyl-1-phenyl or 1,1-dimethyl substitutions in a previous report [22].

In recent years, alcohol or water soluble conjugated polymers have exhibited excellent performances in interfacial modifications of cathodes for PLEDs and PSCs [23]. For instance, the alcohol solubility of a polyfluorene PFN was greatly improved by introducing two *N*,*N*-dimethyl-3-aminopropyl groups to its 9-position [24]. The application of PFN as the interfacial layer of the cathode of PLEDs resulted in powerful electron injections from air-stable high work-function metals (Au, Ag and Al), with device efficiency comparable to those of low work-function metals (Ca, Ba) [25]. For the cathode modifications of normal and inverted PSCs, the open-circuit voltage, short-circuit current, and fill factor, the three photovoltaic parameters for solar cells, could be greatly elevated to give high PSC efficiency of >9% [26–28].

In this work, a new hexaphenylsilole monomer with 2,5-di(4-bromophenyl)-substitutions was successfully synthesized by a lithium naphthalenide-mediated cyclization reaction, in which two 4-(N,N-dimethylamino)phenyl groups were attached to the silicon atom. The resultant monomer 1,1-bis(4-(N,N-dimethylamino)phenyl)-3,4-diphenyl-2,5-bis(4-bromophenyl)silole, was then copolymerized with fluorene monomers [29–31] to afford three different 1,1-bis(4-(N,N-dimethylamino)phenyl)-2,3,4,5-tetraphenylsilole-containing polyfluorenes (PF-N-HPS). Their UV absorption, electrochemistry, and PL properties were characterized. Furthermore, three EL devices with Al, Ba/Al, and TPBI/Ba/Al as the cathodes were applied to evaluate their electron injection and transport properties.

2 Experimental section

2.1 Material

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co., and were used as received. All solvents were carefully dried and distilled under nitrogen flow.

2.2 Synthesis of monomers

Bis(4-(*N*,*N*-dimethylamino)phenyl)-diphenylethynyl-silane (1)

Magnesium powder (480 mg, 20 mmol) was added to a solution of 4-bromo-N,N-dimethylaniline (2.00 g, 10 mmol) in THF (100 mL) under nitrogen atmosphere. The reaction was initiated by iodine (10 mg) at room temperature, and further refluxed under heating for 2 h to provide the crude (N,N-dimethylamino)phenylmagnesium bromide. This Girgnard reagent was added dropwise to solution of tetrachlorosilane (0.63 mL, 5 mmol) in THF (10 mL), and the resulting mixture was stirred for 1 h at room temperature to produce the dichlorosilane. Meantime, phenylethynyl lithium was prepared in another reaction flask as followed. To a solution of phenylacetylene (1.1 mL, 10 mmol) in THF (20 mL) was added *n*-butyl lithium (4 mL, 2.5 M solution in hexane) dropwise at 0 °C, and the reaction mixture was stirred at this temperature for 1 h. With both the dichlorosilane and phenylethynyl lithium in hand, the desired diaryl-bis(phenylethynyl)silane 1 could be assembled. The phenylethynyl lithium mixture was added dropwise to the dichlorosilane solution, and the reaction was performed for 1 h at room temperature. An aqueous solution of HCl (1 M) was added and the mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over MgSO₄. The solvents were concentrated by vacuum evaporation and the crude product was purified by silica gel chromatography using ethyl acetate/petroleum ether (1:8, v/v) as eluent to afford a white solid (1.43 g, 61% yield), which was further purified by recrystallization in toluene/ *n*-heptane to give the title compound **1** (1.21 g). ¹H NMR, (300 MHz, CDCl₃), δ (ppm): 7.74 (d, J = 8.8 Hz, 4H), 7.60 (t, J = 6.3 Hz, 6H), 7.34 (m, 8H), 6.82 (d, J = 9.0 Hz, 4H), 3.00 (s, 12H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 136.18, 132.42, 132.31, 128.76, 128.20, 128.15, 123.06, 111.97, 107.51, 89.55, 40.21.

1,1-Bis(4-(N,N-dimethylamino)phenyl)-3,4-diphenyl-2,5-bis (4-bromophenyl)silole (2)

Granular lithium (84 mg, 12 mmol) was added into a solution of naphthalene (1.58 g, 12.1 mmol) in THF (12 mL), and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 5 h, readily forming lithium

naphthalenide (LiNaph). Then a solution of bis(4-(N,Ndimethylamino)phenyl)-bis(phenylethynyl)-silane 1 (1.41 g, 3 mmol) in THF (5 mL) was added dropwise at 0 °C. The mixture was stirred for 10 min after the ice bath was removed. Then the system was cooled back to 0 °C, ZnCl₂-TMEDA (3 g, 12 mmol) and 20 mL of THF were added. The resulting mixture was stirred for 1 h at this temperature to give the 2,5-dizincated silole intermediate for the following Pd-catalyzed transformation. 4-Bromoiodobenzene (1.7 g, 6 mmol) and PdCl₂(PPh₃)₂ (100 mg, 0.15 mmol) were added to the above reaction mixture, and the system was heated to 50 °C and stirred for 48 h. An aqueous solution of HCl (1 M) was added and the mixture was extracted with diethyl ether. The organic phase was washed with brine and dried over anhydrous MgSO₄ After the solvents were evaporated under reduced pressure, the crude product was purified by silica gel chromatography using ethyl acetate/petroleum ether (1:8, v/v) as eluent to afford a yellow solid (1.31 g, 56% yield), which was further purified by recrystallization in toluene/n-heptane to give the title compound 2 (1.2 g). ¹H NMR, (300 MHz, CDCl₃), δ (ppm): 7.51 (d, J = 8.8 Hz, 4H), 7.11 (d, J = 8.9 Hz, 4H), 7.05 (m, 6H), 6.86(m, 4H), 6.77(m, 8H), 3.01 (s, 12H). $^{13}{\rm C}$ NMR (75 MHz, CDCl₃), δ (ppm): 155.83, 151.57, 139.83, 139.03, 138.73, 137.21, 136.88, 130.82, 129.91, 127.54, 126.38, 119.31, 115.48, 112.11, 40.00.

2.3 Synthesis of copolymers

All polymerizations were carried out by palladium(0)catalyzed Suzuki coupling reactions of the diboronic ester monomer **3** with one equivalent of combined dibromo monomers **2** and **4** under nitrogen protection (Scheme 1). All monomers were purified by recrystallization. Three different ratios of fluorene monomers to the silole monomer (99:1, 90:10, and 80:20) were investigated. A tpytical procedure for the polymerization of PF-N-HPS20 is given below.

Carefully purified 2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-9,9-dioctylfluorene 3 (642 mg, 1 mmol), 2,7-dibromo-9,9-dioctylfluorene 4 (328 mg, 0.6 mmol), 1,1-bis(4-(N,N-dimethylamino)phenyl)-3,4-diphenyl-2,5-bis (4-bromophenyl)silole 2 (169 mg, 0.4 mmol), (PPh₃)₄Pd (6 mg, 0.005 mmol) and several drops of Aliquat 336 were dissolved in a mixture of toluene (10 mL) and aqueous 2 M Na₂CO₃ (2 mL). The mixture was refluxed under nitrogen for 24 h. At the end of the polymerization, a small amount of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9dioctylfluorene was added, and the reaction continued for 12 h to remove the bromine end groups. In a similar way, bromobenzene was added as a monofunctional end-capping reagent to remove the boronic ester end group. The mixture was then poured into vigorously stirred methanol. The precipitate was collected by filtration and washed with acetone to remove oligomers and catalyst residues. The product was dried in vacuum for 24 h to yield PF-N-HPS20 as a yellowgreenish powder (508 mg, 70%). (GPC): M_w 28800; M_w/M_n 1.25 (Table 1). Anal. Calcd. C 88.25, H 9.18, N 1.28; Found: C 86.27, H 9.08, N 1.09.

2.4 PLED fabrication and characterization

Following previously reported procedures, the PLEDs were fabricated with PF-N-HPS1~20 as emissive layers [14]. Patterned indium-tin oxide (ITO; ~15 Ω /square) coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol, subsequently in an ultrasonic bath. After treatment with oxygen plasma, poly(3,4-ethylenedioxythiophene) (PEDOT) was spincoated onto the ITO substrate, followed by drying in a vacuum oven. A thin film of electroluminescent copolymer was coated onto the anode as emissive layer. The TPBI hole blocking layer and metal cathode (Ba/Al or Al) were evaporated on the top of an EL polymer layer in a vacuum coating machine. Currentvoltage (I-V) characteristics of the devices were recorded with a Keithley 236 source meter. The luminance was measured with a calibrated photodiode. The external quantum efficiency was verified by measurement in the integrating sphere (IS-080, Labsphere), and luminance was calibrated by using a PR-705 SpectraScan spectrophotometer (Photo Research).

3 Results and discussion

3.1 Synthesis and characterization

The synthesis of the monomer **2** and polymers PF-N-HPS are shown in Scheme 1. The Grignard reagent prepared from 4-*N*,*N*-dimethylamino-benzene reacted with silicon tetrachloride to give the dichlorosilane intermediate, which was treated with phenylethynyl lithium to afford bis(4-(*N*,*N*-dimethylamino)phenyl)-bis(phenylethynyl)-silane (**1**) in 61% yield. The target monomer 1,1-bis(4-(*N*,*N*-dimethylamino) phenyl)-3,4-diphenyl-2,5-bis(4-bromophenyl) silole **2** was prepared in a one-pot fashion. The cyclization of **1** was accomplished using lithium naphthalenide (LiNaph) at 0 °C to afford 2,5-dilithiosilole, which was readily converted to 2,5-dizincated silole under ZnCl₂-TMEDA conditions. The subsequent selective Negishi coupling reaction with 4-bromo-iodobenzene generated the target monomer **2** in 56% overall yield.

Three different silole-containing polymers PF-N-HPS1, PF-N-HPS10, and PF-N-HPS20 were synthesized from monomer **2** and two 2,7-fluorene monomers (**3** and **4**) by Suzuki coupling reaction in 65–81% yield. The feed ratios of monomer **2** and 2,7-fluorene monomers (the combination of **3** and **4**) were 1%, 10%, and 20% respectively. Light emitting energy transfer conjugated polymers with a random chemical structure demonstrated that the quenching of the light emission of chromophores could be largely suppressed. The average weight molecular weights (M_w) of



Scheme 1 Synthetic routes of the silole monomer and the polymers.

 Table 1
 Molecular weights and elemental analyses of the copolymers

Construction	М	M (M	Elemental analysis ^{a)}			
Coporymer	M _w	$M_{\rm w}/M_{\rm n}$	С	Н	Ν	
PF-N-HPS1	50000	1.78	87.29(89.54)	9.82(10.33)	—	
PF-N-HPS10	30900	1.43	86.74(88.89)	9.44(9.76)	0.64(0.68)	
PF-N-HPS20	28800	1.25	86.27(88.25)	9.08(9.18)	1.09(1.28)	

a) Data given in the parentheses are contents in the feed compositions (leaving groups excluded).

PF-N-HPS1, PF-N-HPS10, and PF-N-HPS20, estimated by gel permeation chromatography (GPC), were 50000, 30900 and 28800 with narrow polydispersity index as 1.78, 1.43 and 1.25, respectively. The elemental analyses of the copolymers are listed in Table 1. The C, H, and N contents of the copolymers are very close to those of the feed compositions (leaving groups excluded).

3.2 UV absorption properties

The UV-vis absorption spectra of PF-N-HPS1, PF-N-HPS10 and PF-N-HPS20 in THF solution are shown in Figure 1. The three different copolymers show similar absorption with absorption maxima around 390 nm, which are mainly attributed to the π - π * absorption of fluorene segment [13]. However, the intensities of absorption edges are



Figure 1 UV absorption spectra of the copolymers in THF solution $(1 \times 10^{-4} \text{ M})$.

obviously different, indicating the influence of silole content. With higher silole content, the absorption at 450 nm increases gradually.

The absorption spectra of the films are very close to those of their THF solutions (data not shown). The optical band gaps of the copolymers are estimated as 2.59, 2.67 and 2.81 eV, based on the onset wavelengths in the absorption spectra of the films (Table 2). With the increase of silole content, the optical band gaps decrease gradually.

3.3 Electrochemical properties

The electrochemical behaviors of the copolymers were investigated by cyclic voltammetry (CV), with the corresponding curves were shown in Figure 2. The CV curves were referenced to a saturated calomel electrode (SCE). The onsets of oxidation potentials (E_{ox}) measured by p-doping scan process are between -5.58 and -5.25 eV. The LUMO levels are calculated based on their HOMO levels and optical band gaps. As listed in Table 2, the LUMO levels are in the range between -2.60 and -2.77 eV.

3.4 Photoluminescence properties

Photoluminescence (PL) spectra of the copolymers are shown in Figure 3. Photoluminescence spectra of the copolymers in a dilute THF solution $(4 \times 10^{-5} \text{ M})$ are shown in Figure 3(a), with the emission maxima listed in Table 3. The PL spectrum of PF-N-HPS1 exhibits only two blue emissive peaks of a polyfluorene at 418 and 440 nm. Because no obvious signature of green emission is observed



Figure 2 Cyclic voltammetry of the copolymer films.



Figure 3 Photoluminescence spectra of the copolymers. (a) THF solution $(4 \times 10^{-5} \text{ M})$; (b) thin solid film. Excitation wavelength: 390 nm.

from HPS segment, the two blue emissive peaks can be ascribed to the low content of silole (1%). The results also indicate that the intrachain excitation energy transfer from fluorene segments to silole units is quite limited in diluted solution. With the increase of HPS contents in PF-N-HPS10 and PF-N-HPS20, a new emissive peak appears at ~506 nm,

 Table 2
 Optical band gaps and electrochemical properties of the copolymer films

Copolymer	Optical band gap (eV)	$E_{\rm ox}\left({ m V} ight)$	HOMO ^{a)} (eV)	LUMO ^{b)} (eV)
PF-N-HPS1	2.81	1.18	-5.58	-2.77
PF-N-HPS10	2.67	0.87	-5.27	-2.60
PF-N-HPS20	2.59	0.85	-5.25	-2.66

a) Calculated according to HOMO = $-e(E_{ox} + 4.4)$; b) calculated from HOMO level and the optical band gap.

with the silole emissions displaying relative intensity of 30% and 60% to the emission of the fluorene segments, respectively. This observation clearly demonstrates the contribution of intrachain excitation energy transfer.

Photoluminescence spectra of the thin solid copolymer films are shown in Figure 3(b), with the PL peaks listed in Table 3. The PF-N-HPS1, with a very low content of silole, still gives a large ratio of emission from fluorene segments. The blue emissive peak is slightly red-shifted, while the green-emissive band from the silole units reaches a relative intensity of 75% in comparison to the emission of fluorene segments, which can be ascribed to the significant contribution of interchain excitation energy transfer in the solid state [13, 14]. For the PF-N-HPS10 with higher silole content on the main chain, the silole emission becomes a major PL peak and the emission from the fluorene segment only displays a 10% relative intensity. In the PL spectrum of PF-N-HPS20 with a silole content of 20%, the emissive band from the fluorene segment almost disappears.

3.5 Electroluminescence properties

Three different PLEDs were prepared with the following configurations: ITO/PEDOT (50 nm)/PF-N-HPS (80 nm)/Al for device A, ITO/PEDOT (50 nm)/PF-N-HPS (80 nm)/Ba/Al for device B, and ITO/PEDOT (50 nm)/PF-N-HPS (80 nm)/TPBI (30 nm)/Ba/Al for device C. In the device C, the TPBI layer was inserted as electron transport and hole blocking material [14]. The EL performances of

 Table 3
 Photoluminescence properties of the copolymers

Caralina	Solution ^{a)}	Film		
Copolymer	λ_{PLmax} (nm)	λ_{PLmax} (nm)		
PF-N-HPS1	418, 440	434, 461, 493		
PF-N-HPS10	418, 440, 506	430, 500		
PF-N-HPS20	418, 440, 508	506		

a) THF solution: 4×10^{-5} mol/L; excitation wavelength: 390 nm

Table 4 EL properties of the copolymers in three device configurations

the three devices are listed in Table 4.

It was reported that the application of polyfluorenes with trialkylamine side chain as the emissive layer in PLEDs with Al cathode could show higher EL efficiency, in comparison to Ba/Al cathode [24, 25]. This was attributed to the formation of interfacial dipole between the trialkylamine groups of the emissive polymer and the Al cathode, which decreased the barrier height for electron injection. Moreover, efficient electron injection from high work function Au cathode could be achieved [25]. Interestingly, in our work, the turn-on voltages (V_{on}) of PF-N-HPS1~20 in device A all exceed 10 V, and the maximum brightness (L_{max}) values are only 38~116 cd/m², showing very low EL efficiencies (Table 4). The results indicate that 4-(N,N-dimethylamino)phenyl groups on PF-N-HPS failed to achieve good electron injection from the Al cathode. Therefore, the electron injection ability from a high work function metal cathode may be quite different for PF-N-HPS with aromatic amine from those with the trialkylamine groups.

The maximum luminous efficiencies (LE_{max}) in device B are improved in comparison to device A. The LE_{max} values of PF-N-HPS1-20 are 1.44, 0.92, and 0.85 cd/A respectively, which are 4-8 times higher than those of device A. The $V_{\rm on}$ values of device B are all below 5 V, and the $L_{\rm max}$ values are between 1460 and 2260 cd/m². The EL spectra of device B are shown in Figure 4(a). A main EL emission peak (λ_{ELmax}) of PF-N-HPS1 appears at 522 nm (Table 4) due to the emission from HPS units, while a weak emission from fluorene segments still exists. The λ_{ELmax} of PF-N-HPS10 is at 538 nm, with a weak shoulder peak at 600 nm. For the PF-N-HPS20, the λ_{ELmax} moves to 605 nm, with the emissive band at 538 nm becoming a shoulder peak. But in device C, there is no emission peak at ~600 nm (Figure 4(b)). Therefore, the emission peaks at ~600 nm may be resulted from the possible interactions between the polar N,N-dimethylamino groups on the silole and the Ba cathode. The electron deficient silole rings could act as effective electron traps, causing exciton recombination zone much close to the cathode [14].

Device configuration ^{a)}	Emissive layer	$V_{\text{on}}^{b)}$ (V)	$\lambda_{\rm ELmax}$ (nm)	η_{ELmax} (%)	$LE_{max}^{c)}$ (cd/A)	$L_{\rm max}^{\rm d)}$ (cd/m ²)	CIE coordinates (x, y)
A	PF-N-HPS1	10.8	522	0.13	0.33	116	-
А	PF-N-HPS10	10.4	534	0.04	0.12	50	_
А	PF-N-HPS20	10.0	540	0.02	0.06	38	-
В	PF-N-HPS1	4.7	522	0.58	1.44	2260	0.35, 0.47
В	PF-N-HPS10	4.9	538	0.37	0.92	1460	0.40, 0.53
В	PF-N-HPS20	4.5	538, 605	0.34	0.85	1690	0.44, 0.49
С	PF-N-HPS1	8.0	440, 507	1.91	4.78	2070	0.24, 0.36
С	PF-N-HPS10	6.4	520	3.18	7.96	4880	0.31, 0.48
С	PF-N-HPS20	8.1	527	1.82	4.56	1340	0.35, 0.53

a) Device A: ITO/PEDOT (50 nm)/PF-N-HPS (80 nm)/Al, device B: ITO/PEDOT(50 nm)/PF-N-HPS (80 nm)/Ba/Al, device C: ITO/PEDOT (50 nm)/PF-N-HPS (80 nm)/TPBI(30 nm)/Ba/Al. The active area for all devices is 0.17 cm²; b) turn-on voltage; c) maximum luminous efficiency; d) maximum brightness.



Figure 4 EL spectra of PF-N-HPS. (a) Device B; (b) device C.

In device C, a TPBI layer was inserted as electron transport and hole blocking material, separating the emissive layer from Ba/Al cathode. As shown in Figure 4(b), the EL spectra are somewhat similar to the corresponding PL spectra, with the λ_{ELmax} red-shifted to the λ_{PLmax} . In the EL spectrum of PF-N-HPS1, a blue emission from fluorene segments is observed, which is remarkably weakened for PF-N-HPS10 with higher silole content. In the EL spectrum of PF-N-HPS20, this blue emission peak totally disappears, with λ_{ELmax} of 527 nm as the exclusive greenemission from silole units. In comparison with device B, the EL efficiencies of device C are significantly improved. As listed in Table 4, the LE_{max} values of PF-N-HPS1-20 are 4.78, 7.96 and 4.56 cd/A respectively, which are 3-8 times higher than those of device B. Among the three emissive copolymers, PF-N-HPS10 displays the highest η_{ELmax} of >3%, with a V_{on} of 6.4 V and an elevated LE_{max} of 4880 cd/m². The improvement of EL performance in device C can be explained as follows: the insertion of the TPBI layer not only enhanced the electron transport and hole blocking, but also separated the PF-N-HPS emissive layer from the metal cathode, which could greatly suppress the cathode quenching.

4 Conclusion

A new silole monomer, 1,1-bis(4-(N,N-dimethylamino)

phenyl)-3,4-diphenyl-2,5-bis(4-bromophenyl)silole, was prepared from tetrachlorosilane. The copolymerization of this silole with flurorene derivatives was achieved using Suzuki coupling to afford PF-N-HPS1, PF-N-HPS10 and PF-N-HPS20. The HOMO levels of the copolymers are between -5.25 and -5.58 eV. The copolymers show green emissions due to excitation energy transfer from fluorene segments to hexaphenylsilole units. The PLED performances of the polymers were investigated with three different cathode configurations (Al, Ba/Al, and TPB/Ba/Al). The efficiencies with Al as cathode are only 0.06-0.33 cd/A, indicating that the 4-(N,N-dimethylamino)phenyl groups in PF-N-HPS cannot achieve effective electron injection from the Al cathode. With Ba/Al as cathode, the electron injection is improved and the efficiencies are elevated to 0.85–1.44 cd/A. By utilizing the electron transport and hole blocking functions of the TPBI layer, the TPBI/Ba/Al cathode can boost the efficiencies to 4.56-7.96 cd/A. The separation of the emissive layer and metal cathode with the TPBI layer may also suppress exciton quenching at the cathode interface.

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