

ORIGINAL ARTICLE

Synthesis and characterization of novel polymers containing aminophenylsilole

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A series of conjugated copolymers consisting of 9,9-dioctylfluorene units and 1,1-bis(4'-*N,N*-dimethylaniline)-tetraphenylsilole units (APh-TPS) were designed and synthesized by a palladium-catalyzed Suzuki coupling reaction. The chemical structures, electrochemical properties and optoelectronic properties, including the absorption, photoluminescence and electroluminescence (EL), of these copolymers were successfully characterized. EL devices were fabricated in three different configurations: indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid; PEDOT:PSS) (50 nm)/polyfluorene (PF)-APh-TPS (80 nm)/Al (device A), ITO/PEDOT:PSS (50 nm)/PF-APh-TPS (80 nm)/Ba/Al (device B) and ITO/PEDOT:PSS (50 nm)/PF-APh-TPS (80 nm)/1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) (30 nm)/Ba/Al (device C). The EL properties of PF-APh-TPS were clearly improved compared with those of previously reported silole-containing PFs because of the introduction of *N,N*-dimethylaniline. The insertion of a TPBI hole-blocking layer not only elevated the luminous and external quantum efficiencies but also improved the color purity by separating the light-emitting layer from the cathode.

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INTRODUCTION

During the past decade, remarkable progress has been made in polymer light-emitting diodes (PLEDs) because of their potential applications in commercial full-color, flexible and large-area flat panel displays and their low-cost solvent processing.^{1,2} In addition, conjugated polymers offer the advantage of versatile synthetic methods, providing various materials with optimized backbone structures to improve device performance metrics, such as brightness, drive voltage and efficiency.

First, polyfluorene (PF) derivatives and their copolymers have emerged as one of the most promising candidates for the fabrication of commercial PLEDs.³ PFs exhibit high photoluminescent (PL) and electroluminescent (EL) efficiencies, high solubility in common solvents and easy modification.³ PFs are typically used to construct backbones with narrow-bandgap moieties to tune the emission color,^{4–12} resulting in various light-emitting materials throughout the entire visible region. In this work, PFs were chosen as the main chain to embed silole derivatives to construct green-emitting materials.

Second, silole is a five-membered silacyclic and has high electron acceptability and fast electron mobility because of the low-lying lowest unoccupied molecular orbital (LUMO) levels that arise from the $\sigma^*-\pi^*$ conjugation formed by the interaction between the σ^* bonds of the silicon atoms and the π^* orbital of the butadiene moiety.^{6,13–17} Both amorphous and crystalline silole films exhibit unique behaviors,^{18–23} including a high PL quantum yield (up to 100%).^{21,23} In particular, 2,3,4,5-tetraphenylsiloles, such as 2,3,4,5-tetraphenylsilole (TPS) and 2,5-dithienyl-3,4-diphenylsilole (TST), exhibit aggregation-induced

emission properties that may overcome the problem of EL quenching caused by molecule aggregation.¹⁹ Furthermore, enhanced emission and balanced transport of holes and electrons have also been observed in silole-based materials.^{18,23} Therefore, TPSs can be incorporated into PFs as narrow-bandgap building blocks to synthesize green-emission polymers, exploiting the advantages of both building blocks.^{6,8,12}

Third, the injection of charge carriers is a crucial factor for the most important PLED parameters, including the efficiencies, turn-on voltage and operating lifetime.^{24,25} Low-work function metal cathodes, such as Ca or Ba, are generally necessary for electron injection in common light-emitting polymers.²⁶ However, low-work function metals are usually sensitive to moisture and oxygen.²⁶ Modifying the surfaces of environmentally stable high-work function metal cathodes, such as by synthesizing ammonium-functionalized PF derivatives,^{27–32} has also been recently reported.^{27–38} Through use of these ammonium-functionalized PF derivatives as the interfacial layer, electron injections from air-stable, high-work function metals (Au, Ag and Al) have been significantly improved, resulting in device efficiencies comparable to those of low-work function metals (Ca and Ba) because of the formation of an interface dipole layer through strong interactions with the metal surface and alignment of the amino group.^{13–18,31,32} However, light-emitting copolymers containing aminoalkyl-substituted 1,1-dimethyl-2,3,4,5-TPS (PSP) have rarely been reported.

In this work, we synthesized a new type of aminophenyl-substituted PSP (1,1-bis(4'-*N,N*-dimethylaniline)-TPS, APh-TPS). This silole was used to construct a series of 2,7-fluorene-based copolymers, namely,

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PF-Aph-TPS, by a palladium-catalyzed Suzuki cross-coupling reaction to obtain green EL emission. The ultraviolet–visible (UV) absorption, electrochemical, PL and EL properties were investigated. Three types of devices with Al, Ba/Al and TPBI/Ba/Al cathodes were fabricated, and the effects on device performance are discussed.

MATERIALS AND METHODS

Instrumentation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 300 (Billerica, MA, USA) spectrometer with tetramethylsilane as the internal reference. The molecular weights of the polymers were obtained with a Waters GPC 2410 (Milford, MA, USA) using a calibration curve of polystyrene standards with tetrahydrofuran as the eluent. UV absorption spectra were recorded on an HP 8453 spectrophotometer (Santa Clara, CA, USA). The PL spectra of the copolymer were obtained on a Jobin Yvon Fluorolog-3 spectrofluorometer (Paris, France). The PL quantum yields of the copolymer films were determined in an Integrating Sphere IS080 (LabSphere; North Sutton, NH, USA) with 405-nm excitation using a HeCd laser (Melles Griot; Rochester, NY, USA). The film PL spectra and EL spectra were recorded on an Instapeck IV CCD spectrophotometer (Oriel Co.; Stratford, CT, USA). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation (Shanghai, China) with platinum electrodes against a saturated calomel reference electrode at a scan rate of 50 mV s^{-1} with a nitrogen-saturated solution of 0.1-M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). The polymer thin-films were deposited on a platinum working electrode.

Materials

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 purified under nitrogen flow.

Synthesis of monomers

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) and 2,7-dibromo-9,9-dioctylfluorene (**3**) were prepared according to the literature³⁹ and recrystallized to achieve the desired purity for the subsequent reactions.

1,1-Bis(4'-*N,N*-dimethylphenylamine)-3,4-diphenyl-2,5-di(4'-bromophenyl)silole (**1**) was prepared from bis(4'-*N,N*-dimethylphenylamine)-diphenylethynylsilane following previously reported procedures.⁸ ^1H NMR, (300 MHz, CDCl_3), δ (p.p.m.): 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) and 3.01 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3), δ (p.p.m.): 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 and 40.00.

Synthesis of copolymers

All polymerizations were synthesized by a palladium(0)-catalyzed Suzuki coupling reaction with an equivalent molar ratio of the diboronic ester monomer to the dibromo monomers under dry argon. All monomers were purified by recrystallization. The molar ratio of fluorene moieties to TPS were 99:1, 95:5 and 50:50. A typical procedure for the polymerization is described below.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (642 mg, 1 mmol), 1,1-bis(4'-*N,N*-dimethylphenylamine)-3,4-diphenyl-2,

5-di(4'-bromophenyl)silole (782 mg, 1 mmol), $(\text{PPh}_3)_4\text{Pd}(0)$ (6 mg, 0.005 mmol) and several drops of Aliquat336 were dissolved in a mixture of toluene (10 ml) and aqueous 2-mol l^{-1} Na_2CO_3 (2 ml). The solution was refluxed under a nitrogen atmosphere 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)-9,9-dioctylfluorene was added to remove the bromine end groups. The reaction was allowed to continue for 12 h. 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 precipitated solid was filtered and washed with acetone to remove oligomers and catalyst residues. The product was dried under vacuum for 24 h to yield a yellow–green powder of PF-Aph-TPS50 (658 mg, 70%). (GPC): M_w , 26 000; M_w/M_n , 1.31 (Table 1). ^1H NMR (300 MHz, CDCl_3), $\delta=7.67$ (d, 4H), 7.58 (d, 2H), 7.49 (d, 4H), 7.36 (d, 4H), 7.10 (m, 10H), 7.00 (s, 4H), 6.80 (d, 4H), 3.01 (s, 12H), 2.00 (s, 4H), 1.27–1.05 (m, 24H) and 0.81 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3), $\delta=155.03$, 151.47, 139.82, 139.52, 139.12, 139.00, 138.08, 137.44, 137.02, 131.00, 130.13, 129.86, 127.57, 126.53, 126.22, 125.49, 120.79, 119.72, 114.14, 112.17, 55.14, 40.60, 40.10, 31.74, 30.00, 29.22, 24.95, 23.75, 22.57 and 14.08.

PLED fabrication and characterization

The PLEDs were fabricated in three configurations: indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (ITO/PEDOT:PSS) (50 nm)/PF-Aph-TPS (80 nm)/Al (device A), ITO/PEDOT:PSS (50 nm)/PF-Aph-TPS (80 nm)/Ba/Al (device B) and ITO/PEDOT:PSS (50 nm)/PF-Aph-TPS (80 nm)/TPBI (30 nm)/Ba/Al (device C). The polymers were dissolved in toluene and filtered through a $0.45\text{-}\mu\text{m}$ filter. Glass substrates patterned with ITO ($\sim 15\Omega$ per square) were cleaned successively with acetone, detergent, distilled water and 2-propanol in an ultrasonic bath. After an oxygen plasma treatment, 50 nm of PEDOT:PSS (Baytron P 4083, Bayer AG) was spin-coated onto the ITO substrate and then dried in a vacuum oven at $80\text{ }^\circ\text{C}$ for 8 h. A thin EL copolymer film was coated onto the anode by spin-casting inside a nitrogen-filled dry box. The film thickness of the active layers was ~ 80 nm, as measured with an Alfa Step 500 surface profiler (Tencor; Milpitas, CA, USA). A thin layer of Ba and a layer of Al were successively evaporated on top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. For device A, only a layer of Al was evaporated on top of the polymer layer. The device performance was measured inside a drybox (Vacuum Atmospheres). The external quantum efficiency was verified by using an integrating sphere (IS080, Labsphere), and the luminance was calibrated by using a PR-705 SpectraScan spectrophotometer (Photo Research; Los Angeles, California, USA) after encapsulating the devices with a UV-curing epoxy and a thin cover glass.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis route is shown in Figure 1. Monomers **1**, **2** and **3** were synthesized following previously reported procedures.^{8,39} All monomers were recrystallized to achieve the required purity for copolymerization.

Copolymers PF-Aph-TPS were synthesized by palladium(0)-catalyzed Suzuki coupling reactions using equimolar diboronic ester monomers (**2**) and dibromo monomers (**1** and **3**). The chemical structures were confirmed to be the target structure by means of ^1H NMR and ^{13}C NMR (see the experimental section). All the polymers were soluble in common solvents, such as chloroform, toluene and

Table 1 Properties of the polymers in solid films

Copolymer	M_w	PDI	Optical bandgap (eV)	E_{ox} (V)	HOMO (eV)	LUMO (eV)
PF-Aph-TPS1	50 000	1.78	2.81	1.18	-5.58	-2.77
PF-Aph-TPS5	55 500	1.67	2.72	1.16	-5.56	-2.84
PF-Aph-TPS50	26 000	1.31	2.15	0.63	-5.03	-2.88

Abbreviations: Aph-TPS, 1,1-bis(4'-*N,N*-dimethylaniline)-tetraphenylsilole units; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; PDI, polydispersity index. The optical bandgaps of the copolymers were estimated from the onset wavelengths of optical absorptions and listed in Table 1. The optical bandgap decreases as TPS contents increasing due to the narrow bandgap of silole units.⁴¹

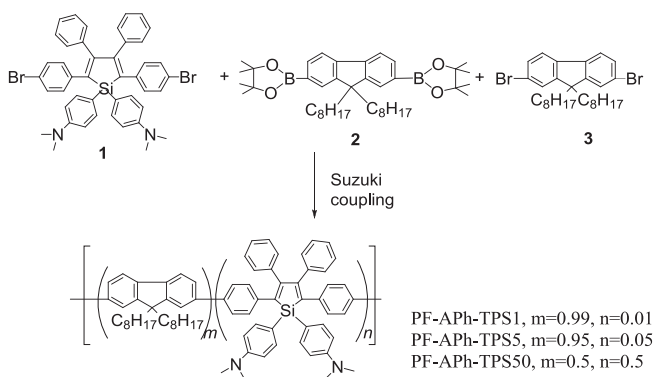


Figure 1 Synthetic route used for the monomers and polymers.

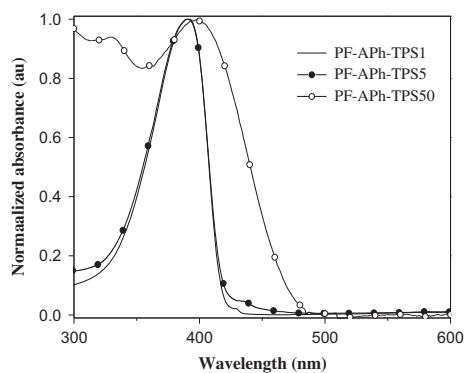


Figure 2 UV absorption spectra of the copolymers.

tetrahydrofuran. The molecular weights of the copolymers are listed in Table 1. The weight-averaged molecular weights (M_w) were between 26 000 and 50 000 with narrow polydispersity indexes between 1.31 and 1.78. The calculated yields were 65–81%.

UV absorption

The UV absorption spectra of the copolymers are shown in Figure 2. The absorption peaks of PF-Aph-TPS1 and PF-Aph-TPS5 were at 390 nm.⁴⁰ There was no silole absorption peak because the silole content was low in PF-Aph-TPS1 and PF-Aph-TPS5. The spectrum of PF-Aph-TPS50 showed a broad peak with a 10-nm red shift because of the formation of alternating polymers and the mixed electronic configurations of both components. The spectrum also exhibited a clearly red-shifted absorption edge, reflecting the contribution of small bandgap silole rings to the electronic transition of copolymers. The absorption maximum of PF-Aph-TPS50 was at 398 nm, which is consistent with previously reported results.⁸

The optical bandgaps of the copolymers were estimated from the onset wavelengths of optical absorptions and are listed in Table 1. The optical bandgap decreased as the TPS contents increased because of the silole units' narrow bandgap.⁴¹

Electrochemical properties

The electrochemical behavior of the copolymers in thin films was investigated by cyclic voltammetry. The measurements were performed in 0.1-mol l^{-1} $n\text{-Bu}_4\text{NPF}_6$ acetonitrile solution at room temperature. The cyclic voltammetry curves shown in Figure 3 were referenced to a saturated calomel electrode (SCE). According to an empirical relation, the highest occupied molecular orbital (HOMO) and LUMO of a conjugated polymer are each approximately 4.4 eV

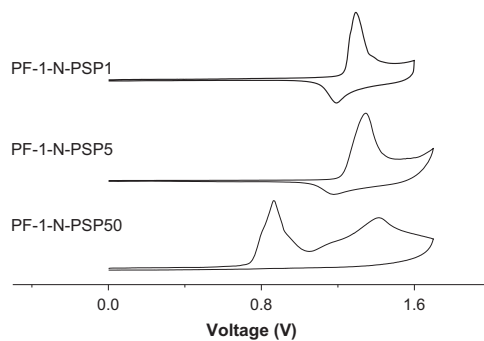


Figure 3 cyclic voltammeters of the copolymers.

(that is, the SCE energy level below the vacuum level) higher than the onset oxidation potential (vs SCE) and the onset reduction potential (vs SCE), respectively.⁴² As shown in Figure 3, the p-doping processes of PF-Aph-TPS1–5 were partially reversible, whereas the p-doping processes of PF-Aph-TPS50 were irreversible. The onsets of the oxidation potentials (E_{ox}) of PF-Aph-TPS1–5 were ~ 1.17 V (Table 1), lower than those of the fluorene homopolymers.^{43,44} In addition, the spectrum of PF-Aph-TPS50 showed a much lower E_{ox} of 0.63 V and two well-resolved oxidation waves at 0.86 and 1.41 V. The newly appearing wave may be attributed to the oxidation of the TPS unit. The HOMO and LUMO of the copolymers were calculated according to the empirical formula $E_{HOMO} = -e(E_{ox} + 4.4)$ eV.⁴⁵ The LUMO was calculated using the HOMO and the optical bandgaps.⁴⁶ The results are listed in Table 1.

PL properties

The PL spectra of these copolymers in tetrahydrofuran solutions at a concentration of $4 \times 10^{-5} \text{ mol l}^{-1}$ are shown in Figure 4a. The PL spectra of PF-Aph-TPS1 and PF-Aph-TPS5 showed main peaks at 418 nm and vibronic peaks at 440 nm resulting from the PF segment.^{6,28} When the silole content was increased to 5%, similarly to previously reported results, a silole-dominant emission peak emerged at 514 nm. When the silole content was increased to 50%, the fluorene emission disappeared, and the silole emission became dominant because of excitation energy transfer from the PF segments to the silole units.⁸

The PL spectra of the thin solid films are shown in Figure 4b. The spectra of PF-Aph-TPS1 and PF-Aph-TPS5 were quite different. The blue emission of the PF nearly disappeared in the spectrum of PF-Aph-TPS5. The silole emission was continuously red-shifted to 527 nm when the silole content was further increased to 50% because of efficient energy transfer and the aggregation-induced emission property of the silole moiety.

EL properties

The EL devices were fabricated in the following configurations: (A) ITO/PEDOT:PSS (50 nm)/PF-Aph-TPS (80 nm)/Al, (B) ITO/PEDOT:PSS (50 nm)/PF-Aph-TPS (80 nm)/Ba/Al and (C) ITO/PEDOT:PSS (50 nm)/PF-Aph-TPS (80 nm)/TPBI/Ba/Al. The EL spectra are shown in Figure 5. The device performance was tested, and the results are listed in Table 2.

The devices without the low-work function metal Ba (device A) were used to evaluate the interfacial effect between the copolymers and the high-work function metal Al. The spectrum of PF-Aph-TPS1 showed two peaks at 440 and 508 nm. On the basis of the literature, the blue emission peak at 440 nm probably originated from the PF segment, and the green-emission peak at 508 nm may have originated

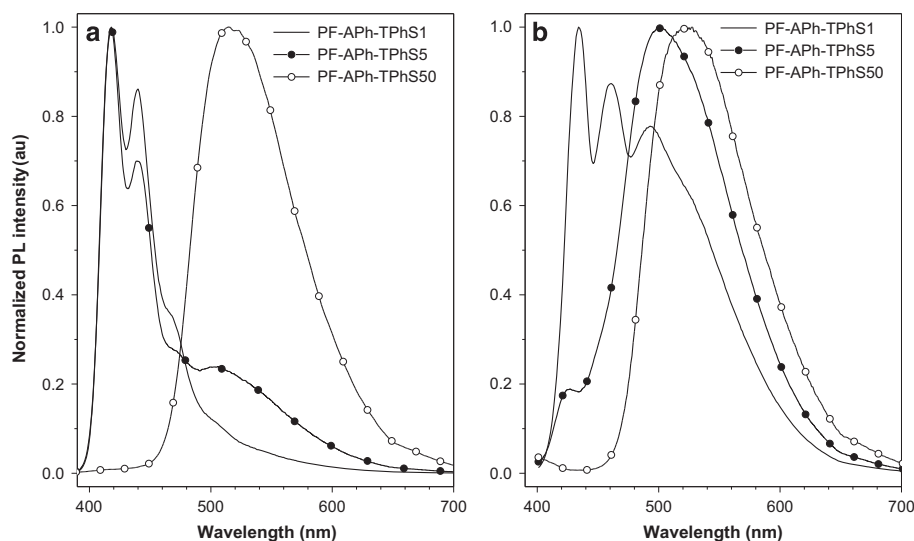


Figure 4 PL spectra of the copolymers (a) in tetrahydrofuran solution ($4 \times 10^{-5} \text{ mol l}^{-1}$) and (b) as thin solid films. Excitation wavelength: 390 nm.

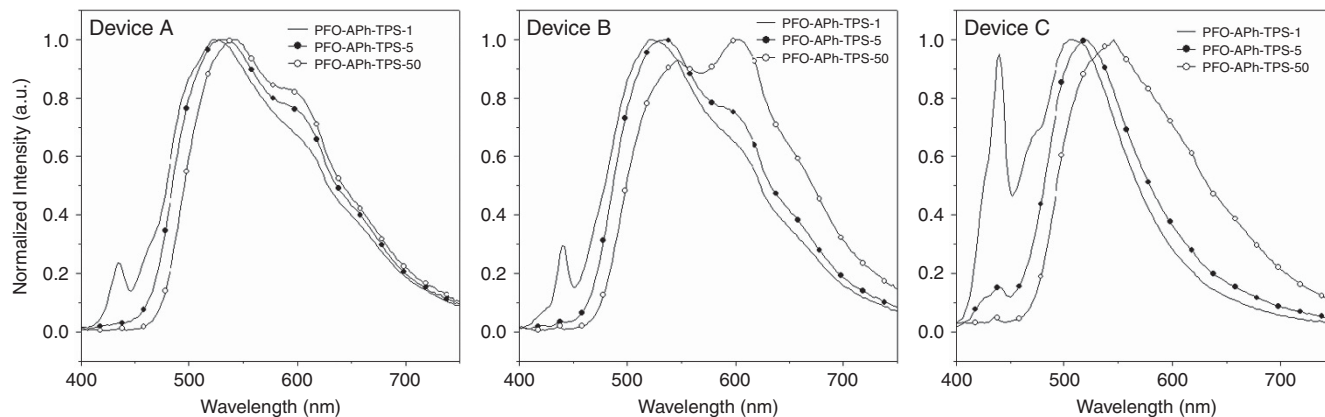


Figure 5 EL spectra with the following device configurations. ITO/PEDOT:PSS/Polymer/Al (device A), ITO/PEDOT:PSS/Polymer/Ba/Al (device B) and ITO/PEDOT:PSS/Polymer/TPBI/Ba/Al (device C).

Table 2 Electroluminescence properties of the copolymers in three device configurations

Device configuration ^a	Emissive layer	V_{on}^b (V)	λ_{ELmax} (nm)	η_{ELmax}^c (%)	LE_{max}^d (cd A^{-1})	L_{max}^e (cd m^{-2})
A	PF-APh-TPS1	10.8	440, 508	0.13	0.33	3.03
	PF-APh-TPS5	11.2	440, 520	0.16	0.40	5.09
	PF-APh-TPS50	10.0	546	0.01	0.02	4.80
B	PF-APh-TPS1	4.7	440, 522	0.58	1.44	2256
	PF-APh-TPS5	4.8	534	0.50	1.24	2363
	PF-APh-TPS50	4.8	546, 600	0.29	0.72	1494
C	PF-APh-TPS1	8.0	434, 522	1.91	4.78	2073
	PF-APh-TPS5	7.9	534	1.64	4.10	1761
	PF-APh-TPS50	7.4	544	1.07	2.68	1600

Abbreviations: APh-TPS, 1,1-bis(4-*N,N*-dimethylaniline)-tetraphenylsilole units; L_{max} , maximum brightness; LE_{max} , maximum luminous efficiency.

^aThe active area for all devices is 0.17 cm^2 . Device A = ITO/PEDOT (50 nm)/ PF-APh-TPS(80 nm)/ TPBI/ Ba/ Al; device B = ITO/PEDOT (50 nm)/ PF-APh-TPS(80 nm)/ Ba/ Al; and device C = ITO/PEDOT (50 nm)/ PF-APh-TPS(80 nm)/ TPBI/ Ba/ Al.

^bTurn-on voltage, defined as the voltage needed for brightness of 1 cd m^{-2} .

^cMaximum external quantum efficiency.

^dMaximum luminous efficiency.

^eMaximum brightness.

from the silole unit.^{6,8} The blue emission peak from fluorene was much weaker than the green emission at a TPS content of only 1%, and it completely disappeared at a TPS content of 5%. Compared with the PL spectra of PF-APh-TPS1 and PF-APh-TPS5, this finding

suggests that TPS units could be efficient exciton traps. As the silole content increased, the fluorene emission disappeared, and the silole peak gradually red shifted to 546 nm. Device efficiencies of only 0.01–0.16% were obtained, corresponding to luminous efficiencies of

0.02–0.40 cd/A and turn-on voltages of 10.0–10.8 V. In some cases,^{30,31} the strong interaction between aminoalkyl moieties and high-work function metals can induce interfacial dipoles, thereby decreasing the turn-on voltages.^{27–32} This might be attributed to the difference between aniline and aminoalkyl moieties, considering that the former is rarely used as the cathode buffer layer. In addition, the shoulder peak at ~600 nm might have arisen from new molecules formed by aluminum ions and *N,N*-dimethylaniline as this shoulder peak increased as the TPS content increased.

Devices with a traditional configuration (device B) were used to evaluate the copolymers' EL properties. Compared with device A, the performance was substantially improved (Table 2). However, the higher TPS content decreased the device performance metrics, such as maximum brightness (L_{\max}) and maximum luminous efficiency (LE_{\max}). The green-emission peak was red shifted from 522 to 546 nm because of the increasing content of narrow-bandgap TPS. An orange emission with a shoulder peak at ~600 nm could also be seen in the spectra of PF-Aph-TPS1 and PF-Aph-TPS5, and became the main peak in the spectrum of PF-Aph-TPS50. This behavior may be attributed to either the stronger interaction between barium ions and *N,N*-dimethylaniline or more efficient electron injection. Notably, this copolymer series resulted in significantly improved device performance compared with that of copolymers consisting of 9,9-dioctylfluorene and 1,1-dimethyl-2,3,4,5-TPS (PFO-PSP) with the same device configuration. In particular, the L_{\max} values of the former were between 1494 and 2256 cd m⁻², which is much higher than the latter's L_{\max} of 256–675 cd m⁻².⁸ The superior results of PF-Aph-TPS may be ascribed to the introduction of 1,1-substituted aminophenyl groups because this is the only difference between the two polymers.

Because the HOMO levels of the copolymers were between –5.58 and –5.03 eV, much higher than TPBI's –6.2 eV, devices with a TPBI hole-blocking layer (device C) were fabricated to generate effective hole blocking. The spectra of device C became sharper, and no orange emission could be seen, indicating that TPBI not only blocks hole transport but also protects the light-emitting layer from being damaged by aluminum or barium atoms during device fabrication or ion diffusion during device operation. The emission peak was also red shifted from 522 to 546 nm. Device C exhibited the highest external quantum efficiencies (1.07–1.91%) among the three configurations and, thus, the highest luminous efficiencies (2.68–4.78 cd A⁻¹). These improved efficiencies and narrower emission bands might be ascribed to the more balanced transport of electrons and holes, which limited the combination zone within the emitting layer.

CONCLUSION

In this study, a series of 1,1-diaminophenyl-silole-modified PFs were copolymerized. The copolymers typically exhibited PF segment-dominated UV absorption behavior. The onsets of the oxidation potentials of these copolymers decreased, and their HOMO levels increased, showing the influence of the silole ring with aminoalkyl groups on the 1,1-positions. The maximum brightness of the device with Ba/Al as the cathode was clearly enhanced (1494–2256 cd m⁻²) compared with that of previously reported silole-containing PFs with an identical device configuration. The insertion of a TPBI hole-blocking layer not only improved the color purity but also elevated the luminous efficiencies and external quantum efficiencies.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

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