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Conjugated random and alternating 2,3,4,5-tetraphenylsilole-containing polyfluorenes: Synthesis, characterization, strong solution photoluminescence, and light-emitting diodes

Feng Wang, Jie Luo, Junwu Chen*, Fei Huang, Yong Cao

Institute of Polymer Optoelectronic Materials and Devices, Key Laboratory of Specially Functional Materials and Advanced Manufacturing Technology of Ministry of Education, South China University of Technology, Wushan Road, Guangzhou 510640, China

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Abstract

A novel series of soluble conjugated random and alternating copolymers derived from 9,9-dioctylfluorene (FO) and 1,1-dimethyl-2,3,4,5-tetraphenylsilole (PSP) were synthesized by Suzuki coupling reactions. The feed ratios of FO to PSP were 95:5, 90:10, 85:15, 70:30, and 50:50. Chemical structures and optoelectronic properties of the copolymers were characterized by elemental analysis, NMR, UV absorption, cyclic voltammetry, photoluminescence (PL), and electroluminescence (EL). The elemental analyses of the copolymers indicated that FO and PSP contents in the copolymers were very close to that of the feed compositions. Unlike the weak PL emission of PSP small molecules in a solution, PFO-PSP solutions could emit strong lights with PL quantum yields between 13 and 30%, indicating that the incorporation of the PSP into the conjugated rigid main chain could greatly restrict the rotations of the phenyl groups of the PSP units even in a solution. Compared with the solution PL, complete PL excitation energy transfer from the PFO segments to the PSP units could be achieved by film PL at lower PSP content. The films of the copolymers exhibited high absolute PL quantum yields between 55 and 84%. EL devices with a configuration of ITO/PEDOT/PFO-PSP/Ba/Al demonstrated that the PSP units could serve as powerful exciton traps, giving exclusively pure green EL emissions. A maximum external quantum efficiency of 1.51% was achieved using the PFO-PSP15 as the emissive layer.

Keywords: Silole-containing polyfluorene; Exciton confinement; Restricted intramolecular rotation

1. Introduction

Since the initial discovery of conjugated polymer electroluminescence (EL) by Burroughes et al. [1], polymer light-emitting diodes (PLEDs) have attracted considerable interest because of their potential application in flat panel displays [2,3]. Ink-jet printing of PLEDs is the key advantage in the commercialization of full-color and large-area flat panel displays [4]. Conjugated polymers can also be applicable in photovoltaic cells (PVCs) [5] and organic field effect transistors (FETs) [6].

Siloles or silacyclopentadienes are a group of five-membered silacyclics that possess unique low-lying LUMO level associated with the σ^*–π^* conjugation arising from the interaction between the σ^* orbital of two exocyclic σ-bonds on the silicon atom and the π^* orbital of the butadiene moiety [7]. Siloles exhibit high electron acceptability [7] and fast electron mobility [8] and have been utilized as electron-transporting and light-emitting layers in the fabrication of EL devices [9–11]. There are great efforts to incorporate siloles into polymers [12–20]. Silole-containing polymers, such as poly(2,5-silole) [12], poly(1,1-silole) [13], silole–thiophene copolymers [14], silole–fluorene copolymers [15,16], silole–acetylene copolymers [17], silole–silane polymers [18], silole side chain polymers [19], and hyperbranched polysiloles [20] have been reported.

In the past decade, polyfluorenes (PFs) have emerged as emitting materials suitable for use in PLEDs because of their highly efficient photoluminescence (PL) and EL, their thermal and oxidative stability, and their good solubility [21–31]. Indeed, among the silole-containing polymers,

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* Corresponding author. Tel.: + 86 20 8711 4346; fax: +86 20 8711 0606.

E-mail address: psjwchen@scut.edu.cn (J. Chen).

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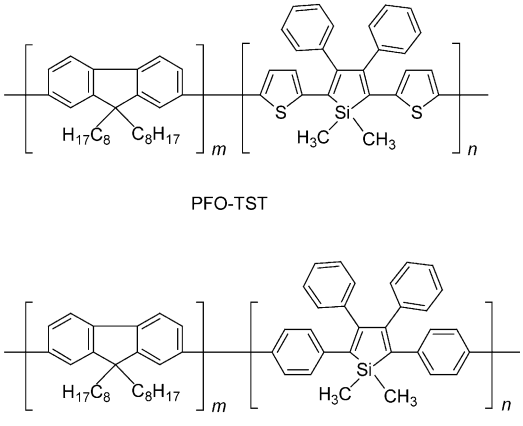


PFO-TST

PFO-PSP

Fig. 1. Structures of PFO-TST and PFO-PSP.

silole–fluorene copolymers have exhibited notable performances in devices such as PLEDs, PVC, and FET [15,16]. Jen and co-workers reported green PLEDs based on random copolymers of 9,9-dihexylfluorene and 4,4-diphenyldithienosilole with low silole content ($\leq 10\%$) [15]. The EL devices demonstrated a maximum external quantum efficiency of 1.64%, which is the highest EL efficiency among all silole-containing polymers. Recently we reported multifunctional performances of random and alternating copolymers of 9,9-dioctylfluorene (FO) and 2,5-dithienylsilole (TST) (PFO-TST, Fig. 1) [16]. PLEDs based on the copolymers emitted red lights. With the alternating copolymer as the electron donor, energy conversion efficiency of 2.01% was achieved under an AM1.5 simulated solar light at 100 mW/cm^2, which is among the highest values so far reported for bulk-heterojunction photovoltaic cells. In a FET device using polyacrylonitrile as an organic insulator on gate electrode, the field effect hole mobility of the alternating copolymer reached 4.5×10^{-5} cm^2/(V s).

2,3,4,5-Tetraphenylsiloles (TPSs) exhibit a novel PL phenomenon of aggregation-induced emission (AIE): The TPSs are practically non-luminescent when molecularly dissolved in good solvents but become highly emissive when aggregated into nanoclusters or fabricated into thin solid films [32,33]. Excellent EL performances with the maximum external quantum efficiency (η_{EL}) up to 8% have been achieved using TPSs as the emissive layer [34,35]. In the previous reports of TPS-containing polymers [13,17–20], TPSs were incorporated into the polymers through the weakly conjugated silicon linkages, not the well-conjugated 2,5-linkages. In this work, we report the synthesis and light emissions of a novel series of soluble conjugated random and alternating copolymers (PFO-PSP, Fig. 1) derived from FO and 1,1-dimethyl-2,3,4,5-tetraphenylsilole (PSP), a TPS derivative. The incorporation of the PSP into the PF main chain can afford an emissive wavelength control, in which the PSP unit can serve as powerful exciton traps, giving exclusively pure green EL emissions. The PSP is almost non-luminescent in a solution due to the rotational deactivation of phenyl groups according to a former report [32], the PFO-PSP solutions, however, can emit strong lights. A possible reason for this is analyzed according to a model of restricted intramolecular rotation [19,32].

2. Experimental

2.1. 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. Compounds bis(phenylethynyl)dimethylsilane (**1**) [36], 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) [21], and 2,7-dibromo-9,9-dioctylfluorene (**4**) [21] were prepared according to the literature, and all of them were recrystallized to reach the desirable purity for the next reactions.

2.2. Instrumentations

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 or AV 400 spectrometer with tetramethylsilane (TMS) as the internal reference. Molecular weights of the polymers were obtained on a Waters GPC 2410 using a calibration curve of polystyrene standards, with tetrahydrofuran as the eluent. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co). UV–vis absorption spectra were recorded on a HP 8453 spectrophotometer. The PL spectra of the copolymer solutions were obtained on a Jobin Yvon Fluorolog-3 spectrofluorometer. The PL quantum yields of the copolymer films were determined in an Integrating Sphere IS080 (LabSphere) with 405 nm excitation of a HeCd laser (Melles Griot). Film PL spectra and EL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against a calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). The deposition of copolymer on the electrode was done by the evaporation of a dilute chloroform solution.

2.3. Synthesis of 1,1-dimethyl-3,4-diphenyl-2,5-bis(4′-bromophenyl)silole (*2*)

A mixture of lithium granular (83 mg, 12 mmol) and naphthalene (1.54 g, 12.1 mmol) in THF (12 mL) was stirred at room temperature under argon for 5 h, readily forming lithium naphthalenide (LiNaph). Then

Table 1
Molecular weights and elemental analyses of the copolymer

Copolymer	M_w[a]	M_w/M_n[a]	Elemental analysis[b]	
			C	H
PFO-PSP5	34,100	1.5	87.27 (89.50)	10.34 (10.14)
PFO-PSP10	33,800	1.6	88.08 (89.38)	10.06 (9.90)
PFO-PSP15	61,300	1.6	88.03 (89.26)	9.88 (9.66)
PFO-PSP30	44,700	1.5	87.49 (88.90)	9.07 (8.96)
PFO-PSP50	21,100	1.5	87.51 (88.48)	8.47 (8.12)

[a] Estimated by GPC in THF on the basis of a polystyrene calibration.
[b] Data given in the parentheses are contents in the feed compositions.

bis(phenylethynyl)dimethylsilane **1** (786 mg, 3.0 mmol) in THF (5 mL) was added to the solution of LiNaph drop-wise over 2 min at room temperature. After stirring for 10 min, the mixture was cooled to 0 °C. $ZnCl_2$(tmen) (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (3.0 g, 12 mmol) was added as a solid to the mixture, followed by the dilution with THF (20 mL), giving a black suspension. After stirring for an additional hour at room temperature, 4-bromoiodobenzene (1.7 g, 6 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) were successively added. The mixture was heated to 30 °C and stirred for 48 h. An aqueous solution of HCl (1 N) was added and the mixture was extracted with ether. The combine extract was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified on a silica gel column using a petroleum ether/carbon tetrachloride mixture (3:1 by volume) as eluent. A green solid of **2** was isolated in 74% yield (1.27 g). Recrystallization from a toluene/heptane mixture gave a pure compound of 1.0 g. ^{1}H NMR (400 MHz, $CDCl_3$), $\delta = 7.26$ (d, 4H), 7.03 (m, 6H), 6.80 (m, 8H), 0.47 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), $\delta = 154.7$, 140.9, 138.8, 138.3, 131.3, 130.5, 130.0, 127.8, 126.7, 119.7, −3.8. GC-mass: *m*/*e* 572 (M^+). Elemental analysis ($C_{30}H_{24}Br_2Si$) (572.4): Calcd. C 62.95, H 4.23; Found C 62.86, H 4.30.

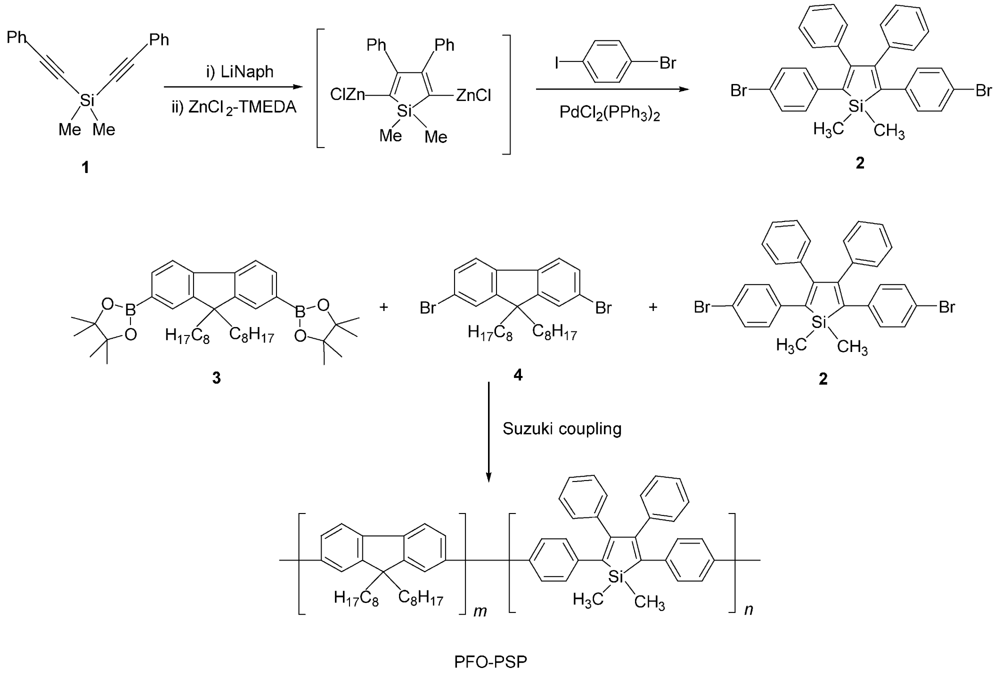
2.4. Polymerization

All of the polymerizations were carried out by palladium(0)-catalyzed Suzuki coupling reactions with equivalently molar ratio of the diboronic ester monomer to the dibromo monomers under dry argon protection. The purifications of the polymers were conducted in air with yields of 70–81%. A typical procedure for the copolymerization is given below.

Carefully purified 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (642 mg, 1 mmol), 1,1-dimethyl-3,4-diphenyl-2,5-bis(4′-bromophenyl)silole (**2**) (572 mg, 1 mmol), $(PPh_3)_4Pd(0)$ (6 mg, 0.005 mmol), and several drops of Aliquat 336 were dissolved in a mixture of toluene (10 ml) and aqueous 2 M Na_2CO_3 (2 ml). The solution was refluxed with vigorous stirring for 24 h. At the end of polymerization, small amount of **3** was added to remove bromine end groups, and bromobenzene was added as a monofunctional end-capping reagent to remove boronic ester end group because boron and bromine units could quench emission and contribute to excimer formation in LED application [37]. The mixture was then poured into vigorously stirred methanol. The precipitated solid was filtered and washed for 24 h with acetone to remove oligomers and catalyst residues. A yellow-greenish powder of PFO-PSP50 was isolated in 78% yield (625 mg). M_w 21,100; M_w/M_n 1.5 (GPC, Table 1). ^{1}H NMR (400 MHz, $CDCl_3$), $\delta = 7.73$ (m, br, 2H, Ar–*H*), 7.52 (m, br, 10H, Ar–*H*), 7.08 (s, br, 8H, Ar–*H*), 6.92 (s, br, 4H, Ar–*H*), 2.00 (s, br, 4H, Ar–CH_2), 1.27–1.05 (m, br, 24H, CH_2), 0.81 (m, br, 6H, C–CH_3), 0.59 (s, br, 6H, Si–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), $\delta = 154.2$, 151.6, 141.2, 140.0, 139.5, 139.1, 138.7, 138.5, 130.0, 129.4, 127.6, 126.6, 126.3, 125.7, 120.9, 119.9, 55.2, 40.6, 31.8, 30.0, 29.2, 25.0, 23.8, 22.6, 14.1, −3.4. Elemental analysis $(C_{59}H_{64}Si)_n$ $(801.2)_n$: Calcd. C 88.44, H 8.05; Found C 87.51, H 8.47. UV ($CHCl_3$): λ_{max} (ε) = 279 (5.4×10^4), 399 nm (1.88×10^4 L mol^{-1} cm^{-1}).

2.5. LED fabrication and characterization

Copolymers were dissolved in toluene and filtered through a 0.45 μm filter. Patterned indium–tin oxide (ITO, ∼15 Ω/□)-coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol, subsequently in an ultrasonic bath. After treatment with oxygen plasma, 150 nm of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) (Baytron P 4083, Bayer AG) was spin-coated onto the ITO substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of electroluminescent copolymer was coated onto the anode by spin-casting inside a nitrogen-filled drybox (vacuum atmosphere). The film thickness of the active layers was around 80 nm, as measured with an Alfa Step 500 surface profiler (Tencor). A thin layer of Ba (4–5 nm) and subsequently 200 nm layers of Al were evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. Device performances were measured inside a drybox (vacuum atmosphere). Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source meter. The luminance of device was measured with 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) after encapsulation of devices with UV-curing epoxy and thin cover glass.



Scheme 1. Synthetic procedures of the copolymers.

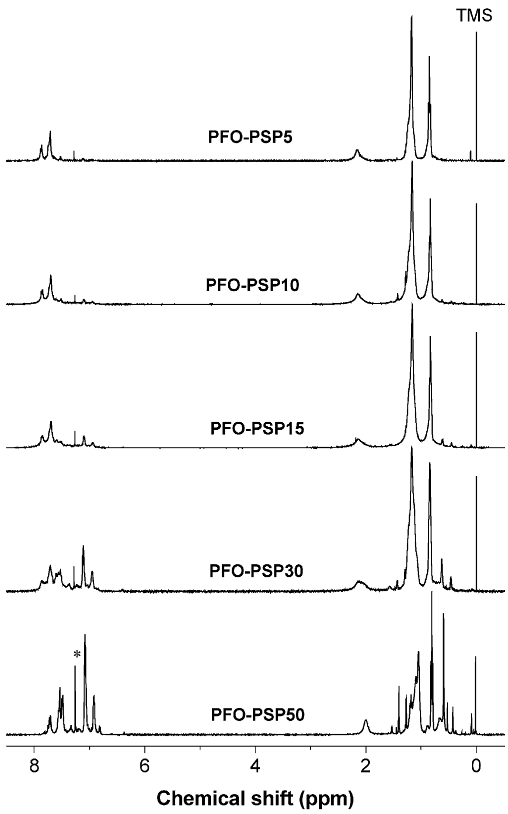


Fig. 2. Evolution of ^{1}H NMR spectra of the copolymers from low TST content to high PSP content. Solvent: $CDCl_3$, the solvent peaks are marked with (*).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedures of the PFO-PSP copolymers are shown in Scheme 1. It is difficult to utilize traditional bromination methods such as NBS [16] and bromine [15,21] to prepare the well-defined dibromosilole monomer **2**, with 1,1-dimethyl-2,3,4,5-tetraphenylsilole as the starting material. Here we designed a one-pot synthetic route for the dibromosilole monomer. We first synthesized 2,5-dizinc silole according to a Yamaguchi method [36]. Due to the higher activity of iodobenzene than bromobenzene in the cross coupling reaction, **2** was prepared by the reaction of 4-bromo-iodobenzene with the 2,5-dizinc silole in a high overall yield of 74% based on diyne **1**. Monomers **3** and **4**, the diboronic ester and dibromo compounds of fluorene, respectively, were synthesized according to a literature [21]. All the monomers were recrystallized to reach the desirable purities suitable for polymerization. Conjugated copolymers derived from monomers **2**–**4** were prepared by palladium(0)-catalyzed Suzuki coupling reactions with equivalently molar ratio of the diboronic ester monomer to the dibromo-monomers. The monomer ratios of fluorene compounds to **2** are 95:5, 90:10, 85:15, 70:30, and 50:50, and the corresponding copolymers are named as PFO-PSP5–50. The PFO-PSP50 is an alternating copolymer and the PFO-TST5–30 are random copolymers. All the copolymers are soluble in common solvents such as chloroform, toluene, and tetrahydrofuran, etc. The molecular weights of the copolymers are listed in Table 1. The M_w

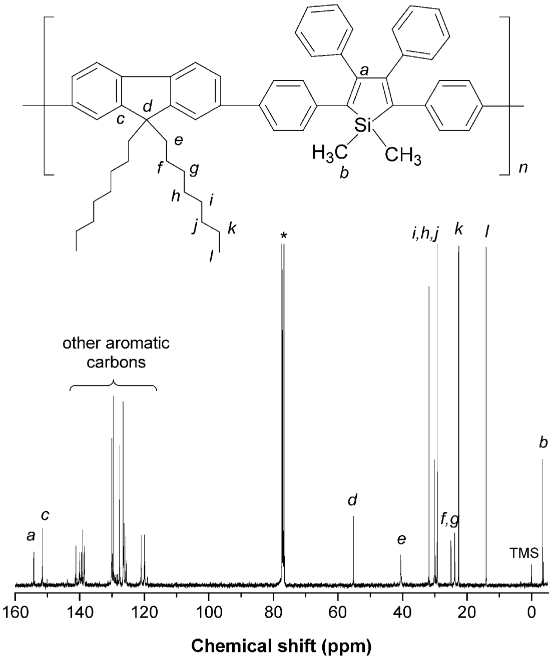


Fig. 3. ^{13}C NMR spectrum of the alternating copolymer (PFO-PSP50) in $CDCl_3$. The solvent peaks are marked with (*).

values of the copolymers are around 2–6×10^4 Da with relatively narrow polydispersity index (M_w/M_n) ($\leq$1.6). The elemental analyses of the copolymers are also listed in Table 1. The contents of C and H of the copolymers are very close to that of the feed compositions.

Fig. 2 shows evolution of ^{1}H NMR spectra of the copolymers from low PSP content to high PSP content. Compared with the ^{1}H NMR spectra, the ^{13}C NMR spectrum of the alternating copolymer, as shown in Fig. 3, is more informative for its chemical structure. The spectrum indicates that the chemical structure of each monomer unit in the alternating copolymer is symmetric. We can assign some characteristic carbon resonance, including one carbon resonating at $\delta=-3.4$ ppm for Si–CH_3 of PSP [16], one carbon resonating at $\delta=154.2$ ppm for 'ene' carbon at 3 or 4-position of the silole ring [38], one carbon at $\delta=151.6$ ppm for 10 or 13-position carbon of fluorene [21], one carbon at $\delta=55.2$ ppm for 9-position carbon of fluorene, and the eight carbons resonating between 40.6 and 14.1 ppm for the *n*-octyl group of the fluorene. The NMR results confirm the chemical structure of the alternating copolymer (see Section 2 for details).

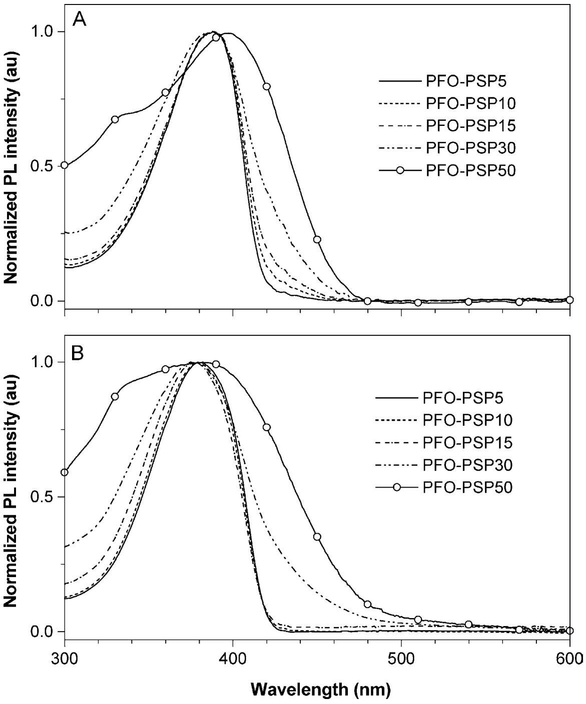


Fig. 4. UV absorption spectra of the copolymers. (A) Chloroform solution (1×10^{-4} M). (B) Thin solid film.

3.2. UV absorption and electrochemical properties

The UV–vis absorption spectra of the copolymers in chloroform solutions are shown in Fig. 4(A). The random copolymers PFO-PSP5–30 show absorption maxima of around 388 nm. The absorption maximum of the alternating copolymer is at 398 nm, with a red shift of 10 nm. The absorption spectrum of PFO-PSP5 is very close to that of PFO homopolymer due to the low content of PSP [16]. Along with the increasing of the PSP contents in the five copolymers, the absorption spectra of the copolymers become broader and the optical absorption edges gradually move to longer wavelengths (~480 nm). Unlike the case of the obvious absorption of the silole unit in a previous report [16], the five copolymers do not show a separate absorption from the PSP unit, indicating that the PSP unit is not such a narrow band gap building block as the 2,5-dithienylsilole (Fig. 1).

The UV–vis absorption spectra of the films of the copolymers are shown in Fig. 4(B). Copolymers PFO-PSP5–15 show comparable absorptions with peaks at ~380 nm and edges at ~430 nm. PFO-PSP30 and PFO-PSP50, with higher PSP contents, also show absorptions at 380–390 nm. Similar to that in solution, the absorption spectrum of the PFO-PSP50 film is the broadest among the copolymers. Its absorption edge is at ~530 nm, showing a red shift of ~50 nm relative to that of the solution absorption, due to the strong intermolecular interaction in the solid state [39].

The electrochemical behaviors of the copolymers were investigated by cyclic voltammetry (CV). For all the copolymers, only one oxidation and one reduction were recorded. The onsets of the oxidation processes for the copolymers are at around 1.32 V, which can be attributed to p-doping of PFO segments corresponding to ionization potential [$\mathrm{IP}=-\mathrm{e}(E_{\mathrm{ox}}+4.4)$] of ~5.72 eV [26]. The onsets of reduction processes of the copolymers are at around −2.3 V, which can be attributed to n-doping of PFO segments corresponding to electron

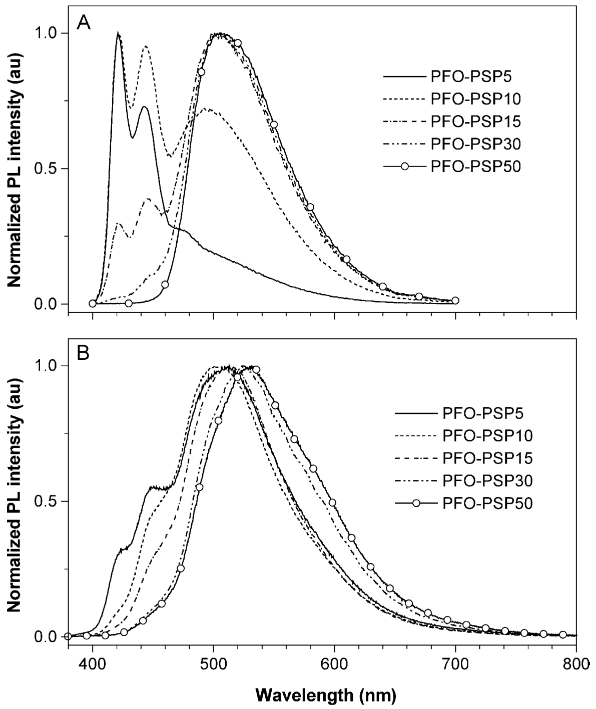


Fig. 5. Photoluminescence spectra of the copolymers. (A) THF solution (4×10^{-5} M). (B) Thin solid film. Excitation wavelength: 390 nm.

affinity [$EA=-e(E_{\mathrm{red}}+4.4)$] of 2.1 eV [28]. Unfortunately, we were unable to record the p- and n-dopings of the PSP unit after many trials. Similar results were reported before [39].

3.3. Photoluminescence property

Photoluminescence spectra of the copolymers in a dilute THF solution at a concentration of 4×10^{-5} M are shown in Fig. 5(A). The PL peaks are listed in Table 2. The PL spectrum of PFO-PSP5 exhibits two well-resolved peaks of PFO emission at 422 and 443 nm, and there is no obvious signature of PSP emission. Since TPS compounds show a larger Stokes shift relative to the PFO and normally emit blue–green lights [32], it can be expected that the PSP emission should be at longer wavelengths compared with the PFO emission. Indeed, for PFO-PSP10, a new emission peak at 493 nm can be observed. For PFO-PSP15, the PFO emission peaks are largely weakened and the PSP emission at 503 nm is dominant. PFO-PSP30 and PFO-PSP50 exhibit exclusively PSP emissions at 504 nm and the PFO emission disappears completely, demonstrating the important role of intramolecular energy transfer from FO segments to PSP units in the PL emission. Similar results were reported for other PF copolymers [16,39].

Table 2
Photoluminescence properties of the copolymers

Copolymer	Solution[a]		Film[b]	
	$\lambda_{\max}$ (nm)	Φ_{PL} (%)[c]	$\lambda_{\max}$ (nm)	QE (%)[d]
PFO-PSP5	422, 443	30	450, 513	65
PFO-PSP10	420, 444, 493	21	501	84
PFO-PSP15	420, 445, 503	17	513	70
PFO-PSP30	504	14	524	77
PFO-PSP50	504	13	531	55

[a] THF solution (4×10^{-5} M); excitation wavelength: 392 nm.
[b] Excitation wavelength: 405 nm.
[c] PL quantum yield using 9,10-diphenylanthracene as reference.
[d] Absolute PL quantum yield measured in the integrating sphere.

Photoluminescence spectra of the thin solid films of the copolymers are shown in Fig. 5(B). The PL peaks are also listed in Table 2. Compared with the PL emission in solution, even for PFO-PSP5 with PSP content as low as 5%, the intensity of the blue emission from PFO segments is largely weakened and the green emission from the PSP units is dominant, due to the contributions of intra- and intermolecular energy transfers in the solid state [16]. With the increasing of PSP content in the copolymers, the blue emission of PFO segments becomes weaker and gradually disappears, along with spectral red shift to 531 nm for PFO-PSP50.

The PL quantum yields (Φ_{PL}) of the copolymers in THF solutions using 9,10-diphenylanthracene as reference are listed in Table 2. The Φ_{PL} of PFO-PSP5 is 30%, much less than that of PFO homopolymer ($\Phi_{\mathrm{PL}}=79\%$) [21]. The PSP is a TPS derivative and shows the AIE phenomenon [32]. Though coplanarity hypothesis was proposed for the AIE mechanism in the beginning [33], the hypothesis was not consistent to the crystal structures of TPS compounds, which showed that the phenyl peripheries of TPS compounds were twisted to a great extents (up to 87°) in the solid state [20,32]. Based on further experimental results of enhanced emissions of TPS solutions upon cooling and thickening, we point out that the faint emission of a TPS compound, with Φ_{PL} as low as ~0.1% in a solution, is due to rotational deactivations of the phenyl peripheries, and the enhanced emissions of TPS aggregates and TPS solutions upon the cooling and thickening are due to the restrictions of the phenyl rotations [32]. Furthermore, restricted intramolecular rotation [19,32], the model for the AIE phenomenon of TPS compounds and TPS-containing polymers, was recently confirmed by time-resolved fluorescence technique [40] and was also applicable for another AIE-active molecule [41]. Thus the lower Φ_{PL} for PFO-PSP5 relative to PFO homopolymer may be attributed to the rotational deactivations of the PSP units in the copolymer. In a solution, the excitation energy from the highly emissive PFO segments is transferred to the less emissive PSP units. The PL quantum yields of PFO-PSP5–50 continuously decrease along with the increasing of PSP content in the copolymers, demonstrating that the extent of rotational deactivations increases with the increasing of the PSP content. The nearly complete energy transfers for PFO-PSP30 and PFO-PSP50 (Fig. 5(A)) and the comparable Φ_{PL} values for PFO-PSP30 and PFO-PSP50 demonstrate that the

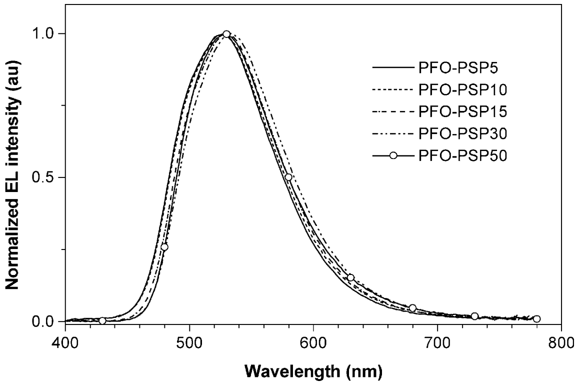


Fig. 6. Electroluminescence spectra of the copolymers.

extents of their rotational deactivations are also comparable. It should be pointed out that the Φ_{PL} of 13% for the PFO-PSP50 solution is much higher than that of PSP small molecules in solution ($\Phi_{PL}=0.11\%$) [32], indicating the extents of the rotational deactivations of PFO-PSP copolymers in solutions are much weaker compared with PSP small molecules in solutions. The Φ_{PL} values for TPS-containing polyacetylenes in solutions are about 0.2% [19] and the value is increased to 1% for hyperbranched TPS polymers [20]. The TPS molecules were attached into the two kinds of TPS-containing polymers through silicon linkages. Their much lower Φ_{PL} values in solutions than that of the PFO-PSP50 solution should be attributed to their much more free rotations of the phenyl groups. In solutions, the phenyl rotations of TPS small molecules and the TPS-containing polymers may be synergistic. The rotations of the phenyl groups in PFO-PSP copolymers should not be so free and synergistic since, each benzene ring at 2,5-positions of a PSP unit is incorporated in the conjugated rigid main chain through the *para*-linkages by a fluorene segment and a silole core. Thus the rotational deactivations are weakened, resulting in the relatively high solution Φ_{PL}. Similar phenomenon was recently found for some well-designed silole small molecules [42].

The absolute PL quantum yields (QE) for the copolymers, measured in an integrating sphere, are also listed in Table 2. The QE for PFO-PSP5 is 65%, slightly higher than that of PFO homopolymer (55%) [43]. The QEs for PFO-PSP10–50 are 84, 70, 77, and 55%, respectively. The high QEs for the copolymers indicate that the extents of the rotational deactivations of PSP units should be greatly restricted in the solid state. The results confirm that the bright green emission, as shown in Fig. 5(B), should mainly come from PSP units due to more efficient intra- and intermolecular energy transfers in the solid state, and should not be caused by the excimer contribution of PFO segments.

3.4. Electroluminescence properties

EL devices with a configuration of ITO/PEDOT (50 nm) /copolymer (80 nm)/Ba/Al were fabricated. The EL spectra of the copolymers are shown in Fig. 6. Even for PFO-PSP5 with only 5% silole, the blue emission from PFO segment almost disappears and the green emission peaks at 524 nm, demonstrating that the silole units are efficient exciton traps. The emission peaks of the other copolymers are at ~528 nm, very close to that of PL spectra of the films of the copolymers with silole contents ≥30%. The PFO-TST copolymers showed red light EL emissions [16]. Our results demonstrate that the incorporation of the PSP into the PF main chain can afford an effective control of the emissive wavelength.

The device performances are listed in Table 3. At a current of ~5 mA, the values of η_{EL} of the copolymers are between 0.35 and 1.11%. Among the copolymers, the device using PFO-PSP15 as the emissive layer shows the best performance, and its maximum η_{EL} is 1.51% at a current of 2.1 mA, which is comparable to the best results reported for silole-containing polymers [15].

4. Conclusions

A novel series of soluble conjugated random and alternating copolymers (PFO-PSP5–50) derived from 9,9-dioctylfluorene and 1,1-dimethyl-2,3,4,5-tetraphenylsilole were synthesized by palladium(0)-catalyzed Suzuki coupling reactions. A facile one-pot synthetic route for the dibromosilole monomer was demonstrated. The solutions and the thin solid films of the copolymers showed PL excitation energy transfer from the PFO segments to the PSP units. The strong green emission from the PSP units of the copolymer solutions suggested that the incorporation of the PSP into the conjugated rigid main chain could greatly restrict the rotations of the phenyl groups of the PSP units.

Table 3
Electroluminescence properties of the copolymers with a device configuration of ITO/PEDOT (50 nm)/copolymer (80 nm)/Ba/Al

Copolymer	Bias (V)	Current (mA)	Brightness (cd/m^2)	η_{EL}[a] (%)	λ_{max} (nm)	CIE x, y
PFO-PSP5	5.95	5.12	351	0.64	528	0.32, 0.56
PFO-PSP10	5.74	5.05	554	0.82	528	0.32, 0.56
PFO-PSP15	6.28	4.87	675	1.11	528	0.34, 0.57
PFO-PSP30	5.45	4.79	323	0.53	534	0.36, 0.57
PFO-PSP50	5.13	5.32	256	0.35	528	0.35, 0.58

The active area is 0.15 cm^2.

[a] The external quantum efficiency.

The restricted rotations were further enhanced in the solid state based on the high absolute quantum yields of copolymer films. EL devices with a configuration of ITO/PEDOT/PFO-PSP/Ba/Al demonstrated that the PSP units could serve as powerful exciton traps, giving exclusively pure green EL emissions. A maximum external quantum efficiency of 1.51% was achieved using the PFO-PSP15 as the emissive layer.

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