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Hole transport triphenylamine–spirosilabifluorene alternating copolymer: synthesis and optical, electrochemical and electroluminescent properties

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Abstract

A new copolymer, constituted by the regular alternation of a spirosilabifluorene with a triphenylamine moiety, P(TPA–SSBF), has been synthesized via Suzuki coupling reaction. The molecular, thermal, optical, electrochemical and electroluminescent properties have been characterized. The introduction of a spiro-structure in P(TPA–SSBF) leads to its high thermal stability and good solubility in common organic solvents. The alternating copolymer shows only an absorption peak of 342 nm, demonstrating that triphenylamine is significantly conjugated with fluorene rings in the polymer. P(TPA–SSBF) in chloroform solution and in solid state film exhibits blue emission peak at 423, 435 nm respectively. The electrochemical behaviors of the polymer were investigated by cyclic voltammetry. The reversible electrochemical oxidation and low ionization potential (5.47 eV) suggest that P(TPA–SSBF) might have potential application as hole transport material in polymer LEDs. The hole transport ability of P(TPA–SSBF) was verified by comparing the performance of the two types LED devices fabricated in this study.

Keywords: Spirosilabifluorene alternating copolymer; Luminescence; Hole-transport

1. Introduction

The development of new charge-transport materials for use in organic light-emitting diodes (OLEDs), organic solar cells, or organic transistors has become a major focus for research in materials science [1–6]. In order to find application in new electronic components, materials have to be developed that form thermally stable amorphous states, having good solubility, and matching the redox levels of the other device components.

Triarylamines have attracted considerable interest as hole transport materials for use in multilayer organic electroluminescence (EL) devices [7–11] due to their relatively high mobilities and their low ionization potentials. The feasibility of utilizing spin-coating and printing processes for large area display devices and possibilities of various chemical modifications make polymers containing triphenylamine (TPA) units very attractive [12–20].

Salbeck et al. introduced the concept of linking two arylamine moieties via a spiro carbon center, introducing a 90° angle between them. This enhances the thermal stability of its amorphous state, without significantly changing their charge-transport properties [1,21–24]. Such spiro- structures have also been applied to polymeric materials, leading to enhancements in glass transition temperature (T_g), solubility and thermal stability [25–31]. Up to now, no triphenylamine–spirobifluorene alternating copolymer has been synthesized. The melting point of 9,9′-spirobifluorene is 198 °C, while 9,9′-spiro-9-silabifluorene (SSBF) is 227 °C. Compared to the compounds containing 9,9′-spirobifluorene, the compounds containing 9,9′-spiro-9-silabifluorene may have an improved morphological stability in films [32–34]. In this work, a novel soluble conjugated alternating copolymer, poly(triphenylamine)-*alt-co*-(9,9′-spiro-9-silabifluorene) (P(TPA–SSBF)), was successfully synthesized by palladium(0)-catalyzed Suzuki coupling reaction. The optical and electronic properties such as UV absorption, electrochemical properties, photoluminescence (PL), electroluminescence (EL) of P(TPA–

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SSBF) were evaluated. To the best of our knowledge, there has not been any report on the spirosilabifluorene-based polymer.

2. Experimental section

2.1. Materials

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. Diethyl ether and tetrahydrofuran (THF) were refluxed with sodium and distilled. All other reagents and solvents were used as received from commercial sources unless otherwise stated.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Brucker AM500 spectrometer with tetramethylsilane (TMS) as the internal reference. Mass spectra were obtained on a VG12-250 mass spectrometer. Molecular weights of the polymer were obtained on a Waters GPC2410 using a calibration curve of polystyrene standards, with tetrahydrofuran as the eluent. Differential scanning calorimetry (DSC) was performed on a DSC2910 using a heating rate of 10 °C/min and a cooling rate of 10 °C/min. Samples were scanned from 25 to 300 °C and then cooled to 25 °C. UV–visible spectra were measured with Varian Cary 500 spectrophotometer. PL spectra were recorded on an Varian Cary Eclipse spectrophotometer. EL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.). Cyclic voltammetry (CV) was carried out on a CHI-800 electrochemical workstation with platinum electrodes at a scan rate of 100 mV/s against a Ag/AgCl reference electrode with a solution of 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile (CH_3CN).

2.2.1. 2,2′-Dibromobiphenyl (**2**)

To a stirred solution of 11.80 g (0.05 mol) of *o*-dibromobenzene in 85 ml of anhydrous THF, cooled to −78 °C, was added 15.8 ml of *n*-BuLi (1.6 M in hexane) over a period of 30 min. The yellow–green reaction mixture was allowed to warm to room temperature and then was hydrolyzed with 40 ml of 5% hydrochloric acid. The resulting layers were separated and the aqueous layer was extracted with ether (20 ml × 2). The ether was combined with the original organic layer and dried over anhydrous sodium sulfate, filtered and concentrated by rotary evaporation. The residue was treated with 12 ml of absolute ethanol and cooled to give 3.4 g 2,2′-dibromobiphenyl. The filtrate was concentrated by rotary evaporation to give 2.0 g additional product. Recrystallization from absolute ethanol gave pure 2,2′-dibromobiphenyl 5.2 g, yield 67%, mp 80–81 °C.

2.2.2. 9,9′-Spiro-9-silabifluorene (**3**)

27 ml of a solution of *n*-BuLi in *n*-hexane (1.6 M) were added dropwise over a period of 5 min to an ice-cooled, vigorously stirred solution of 6 g (19.35 mmol) of 2,2′-dibromobiphenyl in 50 ml of ether and the mixture was subsequently stirred for 2 h at room temperature. A solution of 1.5 g (9 mmol) of silicon tetrachloride in 4 ml of ether was dropwise over a period of 30 min to the mixture and stirred for a further 12 h at room temperature. After shaking with 50 ml of water, the organic phase was dried over magnesium sulfate and filtered, the ether was distilled off on a rotary evaporator. Crystallization from ethanol gave 3.3 g of product, yield 51%, mp 225–227 °C. ^{1}H NMR (500 MHz, CDCl3): δ (TMS, ppm) 7.92 (d, 4H, $J=7.8$ Hz), 7.50 (t, 4H, $J=7.6$, 7.6 Hz), 7.40 (d, 4H, $J=7.1$ Hz), 7.21 (t, 4H, $J=7.2$, 7.2 Hz). EI-MS (*m/z*): 332 (100%).

2.2.3. 2,2′-Dinitro-9,9-spiro-9-silabifluorene (**4**)

1.58 g (6.5 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ are taken up at room temperature using 20 ml of acetic anhydride and stirred. After a few minutes, the blue suspension becoming turbid. 1.0 g (3 mmol) of 9,9′-spiro-9-silabifluorene are added and stirring is continued at 40 °C for 4 h. It is carefully stirred into about100 ml water and shaken with chloroform. The organic phase was separated, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was subsequently reprecipitated from chloroform/hexane, obtained 0.9 g product, yield 75%.

2.2.4. 2,2′-Diamino-9,9′-spiro-9-silabifluorene (**5**)

A mixture of 1.0 g of 2,2′-dinitro-9,9′-spiro-9-silabifluorene and 1.0 g of iron powder were refluxed in 25 ml of ethanol while 4 ml of concentrated hydrochloric acid were added dropwise over a period of 30 min. After refluxing for a further 40 min, excess iron was filtered off. After evaporating the ethanol on a rotary evaporator, 50 ml water was added to the residue. The solution was neutralized dropwise with NH_4OH solution while stirring mechanically and the precipitated product was filtered off with suction. Recrystallization from ethanol afforded 0.65 g white product, yield 76%.

2.2.5. 2,2′-Dibromo-9,9′-spiro-9-silabifluorene (**6**)

2.0 g (5.5 mmol) of 2,2′-diamino-9,9′-spiro-9-silabifluorene are dissolved in 20 ml of water and 5 ml of concentrated hydrobromic acid, cooled to about 0 °C, and slowly admixed with a solution of 0.8 g of $NaNO_2$ in about 5 ml of water while maintaining this temperature. The mixture is stirred at this temperature for about 30 min, and the solution of the resulting bisdiazonium salt is poured into an ice-cooled solution of 1.0 g of CuBr in 10 ml of HBr. The resulting solution is stirred at 100 °C, with gas evolution occurring and the product formed being precipitated as a white deposit. After gas evolution has ended, the product is filtered off with suction, washed with $NaHCO_3$ solution and water. The product is subsequently reprecipitated from chloroform/hexane. Further purification was achieved by using column chromatography on silica gel with a gradient of dichloromethane/hexane to give 1.2 g white solid, yield 45%.

^{1}H NMR (500 MHz, d_6-DMSO): δ (TMS, ppm) 8.12 (d, 2H, $J=7.8$ Hz), 8.08 (d, 2H, $J=8.3$ Hz), 7.75 (dd, 2H, $J=8.3$, 2.0 Hz), 7.60 (t, 2H, $J=7.4$, 7.7 Hz), 7.52 (d, 2H, $J=2.0$ Hz), 7.38 (d, 2H, $J=7.0$ Hz), 7.30 (t, 2H, $J=7.29$, 7.29 Hz). EI-MS (*m/z*): 488 (50%), 490 (100%), 492 (50%).

2.2.6. *N,N-Bis(4-bromophenyl)-aniline*

To a solution of *N,N*-bis(phenyl)aniline (1.23 g, 5 mmol) in DMF (30 ml) was added *N*-bromosuccinimide (NBS) (1.78 g, 10 mmol). The resultant solution was stirred for 20 h at room temperature. The reaction mixture was abstracted with ether. The organic layer was concentrated using rotary evaporation. Further purification was achieved by using column chromatography on silica gel with a gradient of dichloromethane/hexane to yield 1.37 g product as a slight brown, very viscous oil. Yield 90%.

^{1}H NMR (500 MHz, $CDCl_3$): δ (TMS, ppm) 7.35–7.29 (m,4H), 7.28–7.20 (m, 2H), 7.07–7.00 (m, 3H), 6.95–6.90 (m,4H). EI-MS (*m/z*): 401 (50%), 403 (100%), 405 (50%).

2.2.7. *Triphenylamine diboronic acid (7)*

In a 50 ml three-necked flask under an argon flow, 2.0 g (5 mmol) of *N,N*-bis(4-bromophenyl)-aniline was dissolved in 15 ml of anhydrous ether. The solution was cooled to −78 °C and then 9.5 ml (15 mmol) *n*-BuLi (1.6 M in hexane) was slowly added. After 1 h at this temperature, the reaction mixture was allowed to warm gently to room temperature. After cooling to −78 °C, 1.71 ml (15 mmol) trimethylborate was added and the reaction mixture was stirred for 2 days at room temperature. The solution was then washed with diluted hydrochloric acid, water. The organic phase was separated, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatograph (eluent: EtOAc/petroleum ether) to afford 1.1 g yellowish solid. Yield 50%.

^{1}H NMR (500 MHz, d_6-DMSO): δ (TMS, ppm) 7.96 (s, 4H), 7.76 (AA$'$BB$'$system, 4H, $^3J_{HH}=8.4$ Hz), 7.38 (t, 2H), 7.15 (t, 1H), 7.10 (m, 2H), 6.98 (AA$'$BB$'$system, 4H, $^3J_{HH}=8.4$ Hz).

2.3. *Preparation of polymer*

100 mg (0.204 mmol) of 2,2$'$-dibromo-9,9$'$-spiro-9-silabifluorene, 68 mg (0.204 mmol) triphenylamine diboronic acid and 25 mg of tetrakis(triphenylphosphine) palladium(0) were slurried in a mixture of 14 ml of THF and 7 ml of potassium carbonate solution. The mixture was then refluxed under Ar for 3 days. After cooling, the resulting polymer was precipitated into methanol, then washed with water. Soxhlet extraction was performed with methanol and diethyl ether successively to remove oligomers and catalyst residues. The polymer was dried under vacuum to give 70 mg product, yield 75%. $M_w=9577$, $M_w/M_n=1.36$ (GPC). ^{1}H NMR (500 MHz, $CDCl_3$): δ (TMS, ppm) 7.80–6.60 (m, br, 27H, Ar *H*). IR (KBr, cm^{-1}): 3028.6, 1593.1, 1490.5, 1468.3, 1431.0, 1319.6, 1275.8, 821.8.

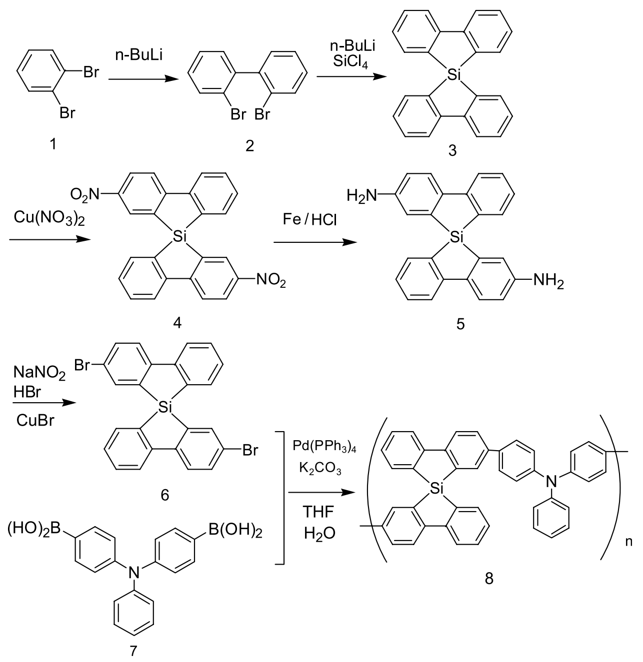
2.4. *LED fabrication and characterization*

Polymer was dissolved in toluene and filtered through a 0.45 μm filter. 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, 60 nm of PEDOT was spin coated onto the ITO substrate followed by drying in a vacuum oven at 80 °C for 8 h. For some devices, poly(vinylcarbazole) (PVK; Aldrich) from 1,1,2,2-tetrachloroethane solution was coated on top of a dried PEDOT layer subsequently. A thin film of electroluminescent copolymer was coated onto the anode by spin-casting inside a nitrogen-filled dry box. 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 dry box (vacuum atmospheres). Current–voltage (*I–V*) characteristics were recorded with a Keithley 236 source meter. The luminance of the device 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 Spectra Scan spectrophotometer (photo research) after encapsulation of the devices with UV-curing epoxy and a thin cover glass.

3. Results and discussion

3.1. *Synthesis and characterization*

The general synthetic routes toward the monomers and polymer are shown in Scheme 1. The dibromo monomer, 2,2$'$-dibromo-9,9$'$-spiro-9-silabifluorene (**6**) was synthesized in five steps starting from 1,2-dibromobenzene (**1**). The preparation of 2,2$'$-dibromo-9,9$'$-spirobifluorene by direct bromination of 9,9$'$-spirobifluorene in the presence of a catalytic amount of ferric chloride has been reported in the literature [35]. However, our attempts to prepare **6** by direct bromination method led to an unexpected compound 4,4$'$-dibromodiphenyl. It can be concluded that this reaction could not be performed using bromine in the presence of ferric chloride as under these conditions the cleavage of the Si–C bond of compound **3** occurred. The structure of compound **6** was verified by ^{1}H NMR spectroscopy as well as mass spectroscopy. Fig. 1 shows the ^{1}H NMR spectra of compound **6**. Based on the ^{1}H NMR data of 9,9$'$-spiro-9-silabifluorene and 2,2$'$-disubstituted-9,9$'$-spirobifluorene



Scheme 1. Synthetic routine of P(TPA–SSBF).

[31], the positions of the chemical shift for protons of compound **6** could be readily assigned as shown in Fig. 1. In addition, the mass spectral data also verified the structure of **6**.

As illustrated in Scheme 1, the triphenylamine–spirosilabifluorene alternating copolymer was prepared from a Suzuki coupling reaction between dibromide **6** and the diboronic acid **7**. The polymerization was carried out in the presence of the larger amount of solvent. The structure of P(TPA–SSBF) was characterized by ^{1}H NMR and IR spectroscopy. The polymer displays a broadening of the ^{1}H NMR signals in aromatic regions. In the IR spectrum, Ar–H bending (821.8 cm^{-1}), Si–Ar (1431.0 cm^{-1}) stretching and C–N (1319.6 cm^{-1}) stretching, corroborate the character of the polymer. P(TPA–SSBF) was readily soluble in common organic solvents, such as THF, toluene, chloroform. The highly soluble nature of this copolymer can be attributed to the presence of the spiro-fused bifluorene segment in the polymer backbone. The molecular weights of the polymer were determined by gel permeation chromatography (GPC) analysis in a THF solution calibrated against polystyrene standards. P(TPA–SSBF) has a M_n of 7014, M_w 9577, with a polydispersity of 1.36. From GPC result, P(TPA–SSBF) has a relative narrow polydispersity index. The reason may be that the polymer has a better solubility in the reaction system. Thus, the reagents can react with each other enough and equably to afford a narrow molecular distribution.

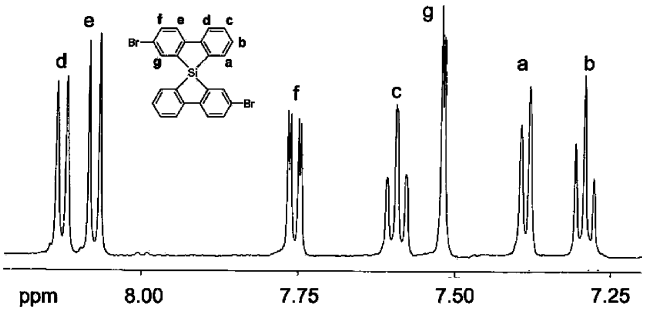


Fig. 1. ^{1}H NMR spectra of compound **6** in d_6-DMSO.

3.2. Thermal properties

The thermal properties of P(TPA–SSBF) was investigated by DSC. DSC was performed in the temperature range from 25 to 300 °C at a heating rate of 10 °C/min. No melting point was observed. A glass transition occurred at 158.2 °C, and a crystallization exothermal peak at 248.9 °C was observed. On subsequent cooling, just the glass transition phenomenon remains in the DSC thermogram. The glass transition phenomenon can be repeated on subsequent heating and cooling cycles and the value of T_g remains within 158.2 ± 1 °C. We note that the exothermal peak appears again when the sample is re-heated. The T_g of P(TPA–SSBF) is significantly higher than many hole transporting materials, such as organosilicon-containing hole transporting material $Ph_2Si(Ph(NPA)_2)_2$ (T_g is 95 °C) [2], hole transporting polymer PPV (T_g is 100 °C) and so on. It is also higher than most fluorene–triarylamine copolymers [15,16]. This comparison illustrates the fact that the incorporation of rigid 9,9′-spiro-9-silabifluorene units into the polymer backbone increases the chain rigidity and results in a higher T_g. The relatively high T_g is essential for polymers as materials in light-emitting applications.

3.3. Electrochemical properties

The electrochemical behavior of P(TPA–SSBF) was investigated by cyclic voltammetry. We could record only p-doping processes and unable to record n-doping processes after many attempts. As shown by the cyclic

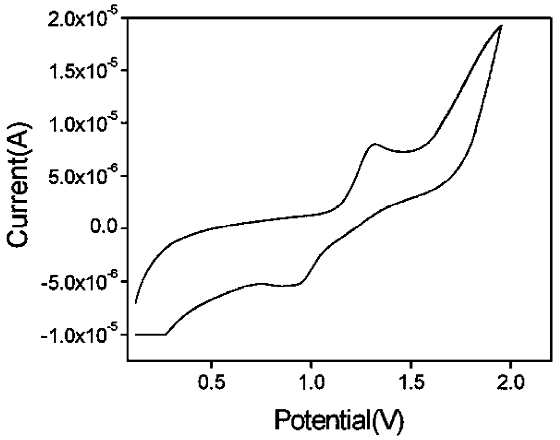


Fig. 2. Cyclic voltammogram of P(TPA–SSBF) in $CH_3CN + 0.1$ M Bu_4NClO_4. Potential Scan rate: 0.1 V/s. The potential was measured relative to Ag/AgCl.

voltammograms in Fig. 2, P(TPA–SSBF) showed reversible p-doping processes. In the anodic scan, the oxidation (p-doping) started at about 1.07 V and gave one corresponding oxidation peak at 1.30 V, which is very close to the data reported for triphenylamine $E_{ox}=0.9$ V and $I_p=5.3$ eV. So the oxidation is attributed to p-doping of triphenylamine segments. The arylamine donor functionality leads to a significant reduction in the oxidation potential. In a comparison with other fluorene–triarylamine copolymers, P(TPA–SSBF) exhibits a lower oxidation potential than poly(fluorene) endcapped triphenylamine and a higher oxidation potential than poly[9,9-bis(triphenylamine) fluorene] [13,15]. It is likely that the oxidation potential of fluorene–triarylamine copolymer decreases with increasing TPA content [16]. The oxidation potential of P(TPA–SSBF) is 0.03 V lower than the widely used hole transporting material PVK [13]. HOMO level calculated according to an empirical formula $\mathrm{HOMO}=-(E_{ox}+4.4)$ eV. HOMO of P(TPA–SSBF) was estimated to be −5.47 eV. The hightlying HOMO energy level and reversible electrochemical oxidation of P(TPA–SSBF) suggest that P(TPA–SSBF) has potential for use as material for hole injection and transport in polymer LEDs [36].

3.4. Optical properties

The UV–vis absorption and PL spectra of P(TPA–SSBF) in chloroform solution at a concentration of around 1×10^{-5} M are shown in Fig. 3. P(TPA–SSBF) shows an absorption due to a π–π^* transition with a λ_{max} at around 342 nm [37]. The band has a 42 nm red-shift relative to that obtained from triphenylamine. The decrease in the π–π^* transition energy is attributed to an increase in the effective conjugation length (increased delocalization) [37]. These results indicate that triphenylamine is significantly conjugated with two fluorene rings in the polymer.

Upon excitation, the solution exhibits a blue PL with only one peak at 423 nm. There is no signature of 9,9′-spiro-9-silabifluorene emission. PL spectrum of P(TPA–SSBF) in thin solid film is shown in Fig. 4. A few changes are denoted when comparing the photoluminescence spectrum obtained in solution and in solid state. The spectrum obtained with the film is of a lower intensity, broadened, red-shifted and shows an additional emission peak at around 495 nm compared to the solution spectrum [38]. The spectral shift observed in the solid state probably is due to the difference in dielectric constant of the environment [13]. The emission peak at around 495 nm probably results from the interchain excimer/aggregate emission [38,39,40]. This phenomenon reveals that chain stacking in the film of P(TPA–SSBF) was not sufficiently suppressed by the spiro segment.

3.5. Electroluminescence properties

Two types of LED devices were fabricated in this study (conditions had not been optimized): ITO/PEDOT/P(TPA–SSBF)/Ba/Al and ITO/PEDOT/PVK/P(TPA–SSBF)/Ba/Al. The structures of LED devices are very similar to those previously reported by Müllen et al. [13]. The PEDOT layer serves as a conductive electrode with work function of around 5.2 eV. In type 1, P(TPA–SSBF) was used as a hole transporting and emitting layer [12]. It is well known that double- and multi-layer LEDs often show better device performance than single-layer LEDs, because of better charge confinement [18]. To verify whether better charge carrier balance is needed, a hole-transport layer PVK (40 nm) with HOMO of −5.50 eV was inserted in type 2 device. Adding PVK also helps in blocking electrons from reaching the anode. In type 1, P(TPA–SSBF) showed the blue emission, which reached a maximum brightness of 8.5 cd/m^2 at 11.7 V. Almost no luminescence was observed in type 2 (Fig. 5(a)). The I–V curves (Fig. 5(b)) for the devices show that the resistance of type1 device was lower than for type 2 device. The highest external quantum efficiency (η) for type 1 device is 0.030%. Type 2 device gives only an highest external quantum efficiency of 0.001%. Since the luminescence and efficiency for type 2 device is not increased but decreased, the addition of a hole

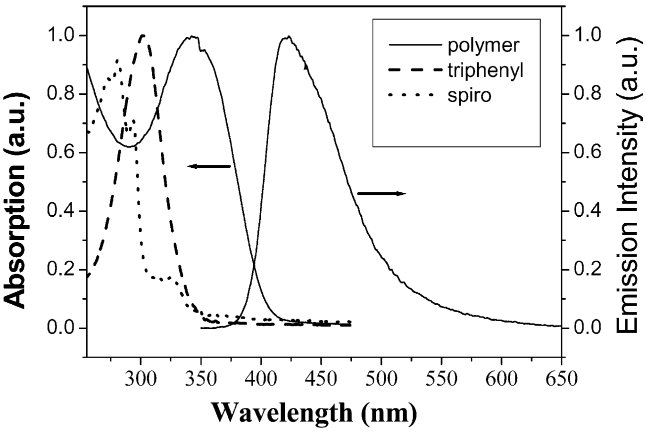


Fig. 3. Absorption and emission spectra of P(TPA–SSBF) in CHCl$_3$ solution (around 1×10^{-5} M).

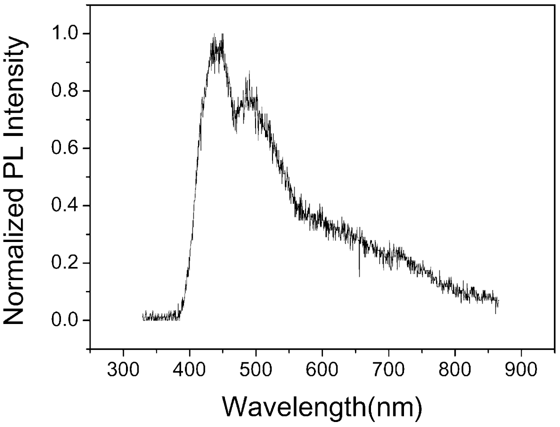


Fig. 4. PL spectrum of P(TPA–SSBF) in solid state film spin-coated on quartz plates.

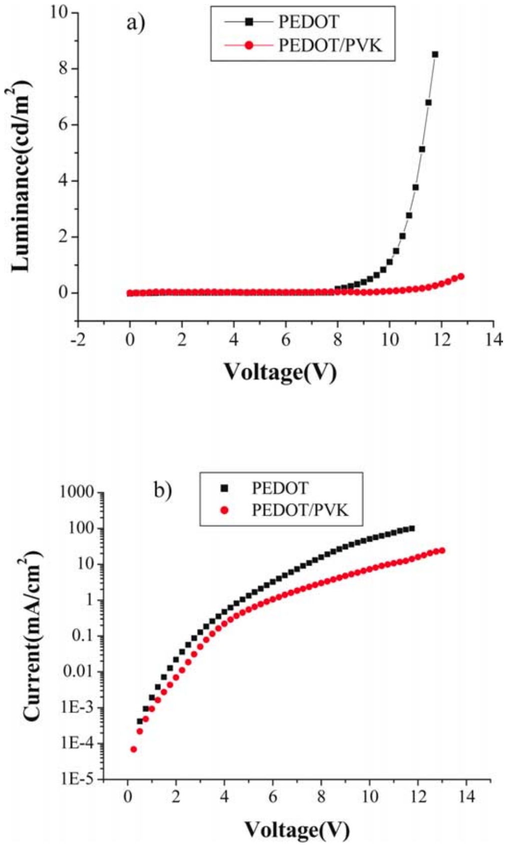


Fig. 5. Luminance (a) and current (b) versus voltages for the devices: ITO/PEDOT/P(TPA–SSBF)/Ba/Al and ITO/PEDOT/PVK/P(TPA–SSBF)/Ba/Al.

transporting layer seems to be unnecessary [13]. The results, together with the hight-lying HOMO energy level and reversible electrochemical oxidation of P(TPA–SSBF), indicate that P(TPA–SSBF) has the ability of hole injecting and transporting [12,13,18,36].

4. Conclusions

In summary, a novel conjugated alternating copolymer P(TPA–SSBF) derived from 2,2′-dibromo-9,9′-spiro-9-silabifluorene and triphenylamine diboronic acid was synthesized by palladium(0)-catalyzed Suzuki coupling reaction. As revealed from the absorption spectra, triphenylamine is significantly conjugated with the fluorene rings in the polymer. Attributed to the spiro structure, P(TPA–SSBF) exhibits a high glass transtion temperature and good solubility. P(TPA–SSBF) possesses reversible oxidation process and low ionization potential (5.47 eV). The hole transport ability of P(TPA–SSBF) was verified by comparing the electroluminescent properties of two types LED devices fabricated in this study. In comparison with the widely used hole transport material PVK, P(TPA–SSBF) exhibits improved solubility and a lower ionization potential. It is expected that P(TPA–SSBF) can be used as hole transporting material in the EL device. Optimal performance of the different structural devices is being done in the progress.

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