



Synthesis and characterization of high triplet energy polyfluorene bearing *m*-tetraphenylsilane segment as a polymer host for green phosphorescent polymer light emitting diodes



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ABSTRACT

A high triplet energy (E_T) copolymer P2SiF, derived from 2,7-fluorene and *m*-tetraphenylsilane segment, was synthesized as a green host for green phosphorescent polymer light emitting diodes. The photophysical properties and device performances of P2SiF were studied and compared with previous P1SiF with 2,7-fluorene and *p*-tetraphenylsilane segment. P2SiF depicted a higher triplet energy level up of 2.60 eV than that of P1SiF, which was probably one of the highest triplet energy from the conjugated polymers with poly(2,7-fluorene) structure. While doped with a green phosphor tris[2-(*p*-tolyl)pyridine] iridium [Ir(mppy)₃], the device hosted by P2SiF showed better performance with a maximum efficiency of 3.36 cd/A as low as doped concentration of 4 wt% Ir(mppy)₃.

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1. Introduction

Organic and polymer light emitting diodes (OLEDs/PLEDs) have currently attracted intensive research activities in both academia and industry because of their potential applications in full-color flat-panel displays and solid-state lighting [1–14]. Compared with OLED based on small molecule emitters, PLED are more suitable for the preparation of large area display due to their allowing inexpensive solution processing technologies, such as spin-coating and ink-jet printing [6–10]. Recently, high efficiency PLEDs based on phosphorescent heavy metal complexes, have drawn great attention due to harvesting both singlet and triplet excitons to realize theoretical 100% internal quantum efficiency [15]. In order to obtain high quantum efficiency for phosphorescent PLEDs (PhPLEDs), heavy metal complexes (such as Ir and Pt complexes) should be dispersed into an appropriate polymer host materials to suppress detrimental processes, such as concentration quenching through triplet–triplet annihilation [16–18]. Thus, the development of suitable polymer host materials is vital for phosphorescent PLED-related research.

An ideal polymer host should satisfy the following conditions: a higher triplet energy level than that of phosphorescent dopant, avoiding energy back transfer from a phosphorescent dopant to a host. Both suitable HOMO/LUMO levels to lower the interfacial energy barriers, a balanced recombination of carriers within the emitting layer, and even high thermal and morphological stability for the thin-film stability of the emitting layer, which are attributed to achieve high efficiency [19–21]. However so far, the search for polymer host with higher triplet energy level, especially for blue PhPLEDs, is still a challenging one, because most conjugated polymers are difficult for hosting blue phosphors due to low triplet energies. Recently, poly(2,7-fluorene)s and their derivatives, owing to wide band gap, high photoluminescence (PL) quantum efficiency, and excellent conductivity, have been most widely used as polymer hosts [22,23]. However, they are not considered as good hosts for blue and green phosphors, due to their low triplet energy (2.15–2.3 eV) [24–26]. As the blue device hosted by poly[(9,9-diethylfluorene-2,7-ylene)diphenylsilylene](PF-Si) while doped with bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (Flrpic) showed a low luminance efficiency of 0.61 cd/A, although over four times higher than those of the poly(9-vinylcarbazole) (PVK) based device with the same configuration [27].

Functionalized tetraphenylsilane materials, were successfully used as blue polymer hosts for high efficiency PhPLEDs, because the introduction of tetraphenylsilane moieties can interrupt the

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δ -Si extended π -conjugation length for high value of E_T and wide band gap [27–29]. However, in these polymer hosts, tetraphenylsilane moiety was mainly based on *p*-tetraphenylsilane. There have been almost no reports on these polymers with *m*-tetraphenylsilane moieties as hosts for doped PhPLEDs, even if few polymers with *m*-tetraphenylsilane derivatives have been previously mentioned as single emitting materials for non-doped PLEDs [30]. We expected the incorporation of *m*-tetraphenylsilane in the polymer skeleton might make polymers with much wider band gap and higher triplet energy level than that for *p*-tetraphenylsilane, due to the δ -Si and *m*-phenylene interrupted π -conjugated length.

In this communication, we reported the synthesis and characterization of an alternating copolymer P2SiF, deriving from 2,7-fluorene and *m*-tetraphenylsilane segment. The photophysical properties and device performances of P2SiF were studied and compared with previous P1SiF with *p*-tetraphenylsilane moiety. P2SiF showed higher triplet energy level up of 2.60 eV than that of P1SiF, which was probably one of the highest triplet energy level from conjugated polymers with poly(2,7-fluorene) structure.

2. Experimental

2.1. Materials and characterization

1,3-dibromobenzene, dichlorodiphenylsilane, 2.5 M *n*-BuLi, 2,7-dibromo-9,9-dioctyl-fluorene, potassium carbonate (K_2CO_3), tetrakis(triphenylphosphine) palladium(0) ($Pd(pph_3)_4$) were purchased from Sigma–Aldrich, TCI, or Acros Organics, and used without any purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether were purified by distillation from sodium in the presence of benzophenone. Other chemicals were used unless otherwise specified.

The 1H NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer. The FT-IR spectra were measured on a Shimadzu 8400S spectrometer. The thermal analyses were performed on Shimadzu DTG-60H thermogravimetric analyzer, in a nitrogen atmosphere at a rate of 20 °C/min. Differential scanning calorimetry (DSC) was conducted under nitrogen on TA DSC2910/SDT2960. The sample was heated at a temperature of 20 °C/min from 30 °C to 250 °C. UV–vis absorption spectra and PL spectra were measured by Shimadzu UV-3100 spectrophotometer and Edinburgh FL/FS920 TCSPC luminescence spectrophotometer, respectively. Molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) analysis, with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, I-Styragel columns of HR4, HR4E, and HR5E with 500 and 100 Å, refractive index detectors, solvent THF). Cyclic voltammetry (CV) was performed on PARSTAT 2273 system, with a three-electrode cell in a solution of Bu_4NBF_4 (0.1 M) in acetonitrile, at a scan rate of 100 mV/s. The polymer films were coated on a square Pt electrode (0.50 cm²) by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode, and an Ag/AgCl (0.1 M) electrode was used as the reference electrode. Prior to each series of measurements, the cell was deoxygenated with nitrogen.

2.2. Synthesis

The (9,9-dioctyl-9H-fluorene-2,7-diyl)diboronic acid was considered according to reference [31]. Bis(3-bromophenyl)diphenylsilane (**3**) was synthesized by the reference [32].

2.2.1. Bis(3-bromophenyl)diphenylsilane (**2**)

1,3-Dibromobenzene (10 g, 40 mmol) and 100 mL of freshly dried diethyl ether were added to a 250 mL 2-necked flask. When

the solution was cooled to 195 K using dry ice/acetone bath, *n*-BuLi (11.7 g, 40 mmol) was injected slowly and stirred for 2 h at 195 K. After the reaction mixture was maintained at 195 K, dichlorodiphenylsilane (5.10 g, 20 mmol) was rapidly injected. Then the reaction mixture was stirred for 10 h at room temperature. After the reaction mixture was poured into water, the product was extracted with diethyl ether and dried over $MgSO_4$. The pure product was obtained by column chromatography using hexane as eluent. Yield: 6.24 g (63%). 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.67 (s, 2H); 7.62–7.60 (d, 2H); 7.56–7.55 (m, 4H); 7.50–7.42 (m, 8H); 7.35–7.31 (t, 2H).

2.2.2. Poly[bis(3-phenyl)diphenylsilane-alt-9,9-dioctyl-9H-fluorene-2,7-diyl] (**P2SiF**)

All handling of catalysts and polymerization was performed in a nitrogen atmosphere. To a stirred solution of **1** (0.38 g, 1.0 mmol) and **2** (0.36 g, 1.0 mmol) in THF, 8 mL of 2 M K_2CO_3 and $Pd(pph_3)_4$ (0.13 g, 0.1 mmol) were added as the catalyst. After the reaction solution was refluxed for 24 h, bromobenzene and phenylboronic acid were added with small amounts of catalysts for end capping. Then, the reaction was terminated with water, extracted with chloroform, and dried over magnesium sulfate. After precipitation was performed twice with chloroform/methanol, the copolymer was obtained. Yield: 0.47 g (65%). 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.95 (m, 2H, Ar-H), 7.82–7.72 (m, 10H, Ar-H), 7.58–7.45 (m, 12H, Ar-H), 2.05–1.98 (m, 4H, CH_2), 1.19–1.05 (m, 20H, CH_2), 0.86–0.84 (m, 6H, CH_3), 0.72–0.69 (m, 4H, CH_2), IR (cm^{-1}): 3065, 2930, 2360, 1460, 1110, 700, Mw: 8888; PDI: 1.85 (GPC).

2.2.3. Poly[bis(4-phenyl)diphenylsilane-alt-9,9-Dioctyl-9H-fluorene-2,7-diyl] (**P1SiF**)

The synthetic method of **P1SiF** was similarly to **P1SiF**. **1** (0.38 g, 1.0 mmol) and **3** (0.36 g, 1.0 mmol) in 30 mL of THF, 8 mL of 2 M K_2CO_3 and $Pd(pph_3)_4$ (0.13 g, 0.1 mmol) were reacted. Yield: 0.43 g (60%). 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.85–7.84 (d, 2H, Ar-H), 7.79–7.74 (m, 7H, Ar-H), 7.69–7.65 (m, 4H, Ar-H), 7.50–7.41 (m, 5H, Ar-H), 7.30 (s, 6H, Ar-H), 2.15 (m, 4H, CH_2), 1.19–1.15 (m, 24H, CH_2), 0.91–0.78 (m, 6H, CH_3), IR (cm^{-1}): 3067, 2920, 2360, 1590, 1110, 810, Mn: 10,587, Mw: 18,239, PDI: 1.72 (GPC).

2.3. Device fabrication

Devices consisting of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/EML (60 nm)/1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl) benzene (TPBI) (40 nm)/LiF (0.5 nm)/Al (120 nm) were fabricated as follows: a 40 nm-thick PEDOT:PSS film was spin-coated onto the cleaned ITO-coated glass substrate from its aqueous solution and then heated at 120 °C for 15 min to remove the residual water solvent. In the PhPLEDs, the emission layer (60 nm), composed of the host material and 1,3-bis[4-*tert*-butylphenyl]-1,3,4-oxadiazolyl-phenylene (OXD-7) as the electron-transporting material by a 10:4 ratio, and phosphorescence dopant (5 wt% or 10 wt%), which was prepared by spin-coating its chlorobenzene solution with a concentration of 15 mg/mL atop PEDOT:PSS layer. After the spin-coating, all devices were transferred into a vacuum chamber immediately without exposure to the atmosphere. Inside the chamber, 40 nm TPBI, 0.5 nm LiF, and 120 nm Al were in sequence deposited by thermal evaporation. The EL spectra and chromaticity coordinates were measured with a SpectraScan PR655 photometer. Current density–voltage–luminance (J – V – L) measurements were conducted simultaneously using a combination of a Keithley source-meter (model 2602) and a calibrated luminance meter. All of the measurements were carried out at room temperature under ambient conditions.

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