Triarylamine-Containing Poly(perfluorocyclobutane) as Hole-Transporting Material for Polymer Light-Emitting Diodes

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Polymer light-emitting diodes (PLEDs) have been the subject of intense research interests recently due to their applications in large-area flat panel displays.[1] To achieve highly efficient PLED devices, charge (holes and electrons) injection and transport from both the anode and the cathode should be balanced at the junction of the emitting layer to yield the maximum exciton formation.[2] In a multilayer PLED, it is highly desirable to develop a suitable hole-transporting layer (HTL) that combines good mechanical properties and thermal and electrochemical stability. Small organic molecules, such as copper phthalocyanine (CuPc) or triarylamines, are very good hole-transporting materials; however, their applications in PLEDs are restrained intrinsically by their physical properties, such as phase separation, erosion, and spectrum absorption and by a sophisticated vacuum evaporation procedure required in device fabrication. On the other hand, commonly used hole-transporting polymers, such as poly(vinylcarbazole) (PVK), suffered from their poor solvent resistance that prevented them from being used efficiently in fabricating multilayer PLEDs. According to the stepwise multilayer PLED spin-casting procedure, the hole-transporting polymer should be dissolved into a solvent to form a homogeneous solution for spin-casting. In addition, the resulting hole-transporting polymer film should be able to withstand the interfacial erosion by organic solvents during the spin-casting of polymer emissive layers thereafter.

Recently, Bellmann et al. had reported that, by using cross-linkable polymers with triarylamine derivatives covalently attached on the polymer backbone, the possible phase separation in guest−host polymer systems was prevented. These polymers were prepared via the ring-opening metathesis polymerization and then cross-linked by UV radiation.[3] However, these polymers possessed relatively low glass transition temperatures (T_g) which may prevent them from being used in LEDs that demand long-term stability.

Herein, we report the synthesis and characterization of a series of highly efficient hole-transporting polymers with triphenylamine (TPA) or *N*,*N*′-bis(4-butylphenyl)-*N*,*N*′-diphenyl-1,1′-diphenyl-4,4′-diamine (di-Bu-TPD) covalently attached, as side chain, on the perfluorocyclobutane (PFCB) backbone.

These polymers were prepared from their corresponding monomers by in-situ curing/polymerization at 225 °C for 1 h under nitrogen. The mechanism to convert a soluble precursor monomer, ditrifluorovinylphenyl ether (DTFVPE), into an insoluble PFCB polymer was reported earlier by Smith et al.[4] These linear polymers can be processed into thin film HTL in sandwiched LEDs by simple thermal cyclopolymerization without introducing any byproducts. Thus, the fabrication of HTL in multilayer PLEDs can be conveniently streamlined as a concise material synthesis and film-casting process. As a result, multilayer device fabrication can be simplified by this maneuver to the converged spin-casting process.

The general methodology for the synthesis of monochloro- and dichloro-substituted organosilane−DTFVPEs **1** and **2** is shown in Scheme 1, using a similar approach developed by Smith et al.[4] DTFVPE−lithium was reacted with chloromethylsilane and dichlorosilane respectively to afford **1** and **2**. *N*,*N*′-bis(4-butylphenyl)-*N*,*N*′-diphenyl-1,1′-diphenyl-4,4′-diamine (di-Bu-TPD) was prepared via the palladium-catalyzed cross-coupling reaction as was reported by Marder et al.[5] Aldehydes were synthesized from TPA and di-Bu-TPD via the Vilsmeier reaction.[6] They were readily reduced by sodium borohydride in THF at room temperature to afford alcohols **3** and **4** in quantitative yield. These hydroxyl-containing TPA and di-Bu-TPD, **3** and **4**, were then condensed with **1** and **2** to obtain the triarylamine-containing DTFVPE **5**−**8**. Linear PFCB polymers **9**−**12** with substituted triarylamines pendants were obtained by in-situ cyclopolymerization of **5**−**8** at 225 °C for 1 h.

Thermal properties of these polymers were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a Shimadzu TA-50 WSI thermal analyzer. The samples were prepared by isothermal heating of the monomers at 225 °C for 60 min before analysis. Electrochemical properties were measured by cyclic voltammetry (CV) using a BAS CV-50W voltammetric analyzer. Thermal and electronic properties of **9**−**12** are summarized in Table 1. These polymers possessed very high decomposition temperatures (T_d's), ranging from 376 to 403 °C. Their glass transition temperatures were between 125 and 150 °C, which were well above device operation temperatures. Good thermal stability of these PFCB polymers may be attributed to the stability of the PFCB backbone. Notably, these PFCB polymer films possessed excellent solvent resistance to dichloroethane (DCE), tetrahydronfuran (THF), and toluene. In addition, results from the CV measurements of the polymer thin films on ITO substrates showed very good reversibility, which were very similar to that of the triarylamine small molecule analogues. Figure 1 shows the CVs of TPD and **10**. Both of them had two reversible peaks under the oxidative process and showed little change after 10 repetitive cycles, indicating their electrochemical stability. The highest occupied molecular orbital (HOMO) levels of **9**−**12**, estimated from the CV measurements, ranged from 5.17 to 5.32 eV below vacuum level (Table 1), which were very close to the work function of ITO glass (about −4.8 eV). This also indicated that these polymers are good hole-injecting materials for PLEDs.

Polymer **12** possessed the highest concentration of the hole-transporting moiety and thus was integrated into a double-layer device to test its efficiency in improving the device performance. In parallel, a single-layer device was also fabricated for comparison. Devices were fab-

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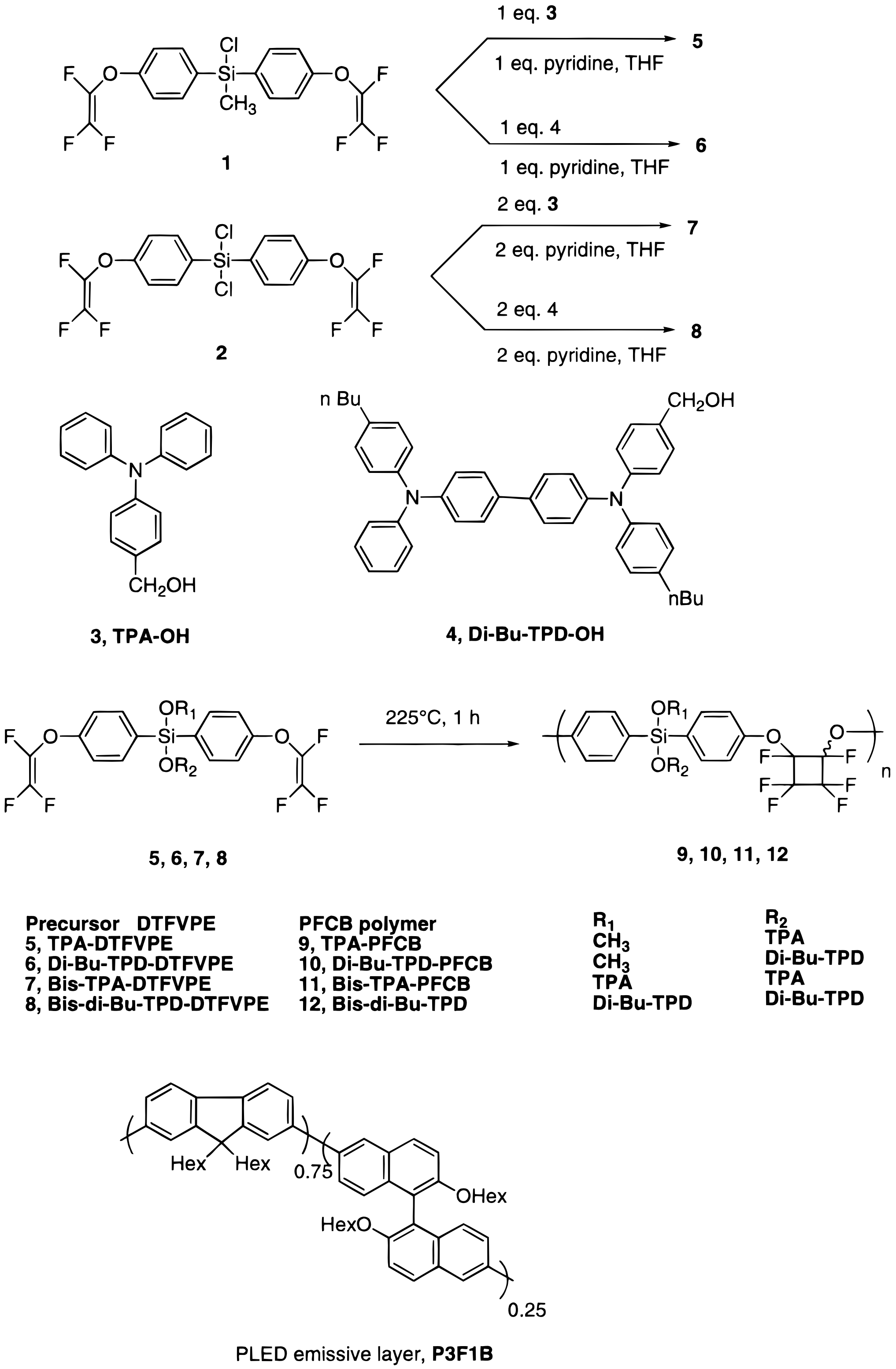
Scheme 1. Synthesis of Triaryl-Containing PFCB Polymers 9−12 and Chemical Structures of Fluorene−Binaphthyl Copolymer, P3F1B



Precursor DTFVPE	PFCB polymer	R_1	R_2
5, TPA-DTFVPE	9, TPA-PFCB	CH_3	TPA
6, Di-Bu-TPD-DTFVPE	10, Di-Bu-TPD-PFCB	CH_3	Di-Bu-TPD
7, Bis-TPA-DTFVPE	11, Bis-TPA-PFCB	TPA	TPA
8, Bis-di-Bu-TPD-DTFVPE	12, Bis-di-Bu-TPD	Di-Bu-TPD	Di-Bu-TPD

ricated on ITO glass substrates with a sheet resistance of ∼65 Ω/□ (Thin Films Corp.) which had been ultrasonicated sequentially in detergent, methanol, chloroform, and acetone before use. Thickness of films was measured on a Sloan Dektak 3030 surface profilometer. Device testing was carried out in air at room temperature. Current−voltage characteristics were measured on a Hewlett-Packard 4155B semiconductor parameter analyzer. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Photometric units (cd/m^2) were calculated using the forward output power and the EL spectra of the devices, assuming a Lambertian distribution of the EL emission.[7] The HTL was fabricated by spin-casting the DCE solution (1−2 wt %) of **12** onto ITO glass substrates and then cured at 225 °C for 60 min under nitrogen. The resulting film with an average thickness of 50 nm was colorless, transparent, and pinhole-free with good mechanical

Table 1. Physical Properties of PFCB Polymers 9−12

polymer	T_g (°C) [a]	T_d (°C) [a]	HOMO (eV) [b]
9	150	400	−5.17
10	125	376	−5.31
11	147	403	−5.18
12	133	380	−5.32

[a] At heating rate of 10 °C/min under nitrogen in DSC analysis. [b] HOMO energy level was calculated by using ferrocene (FOC) value of −4.8 eV below the vacuum level (E_{FOC} = 0.12 V vs Ag/Ag^+).

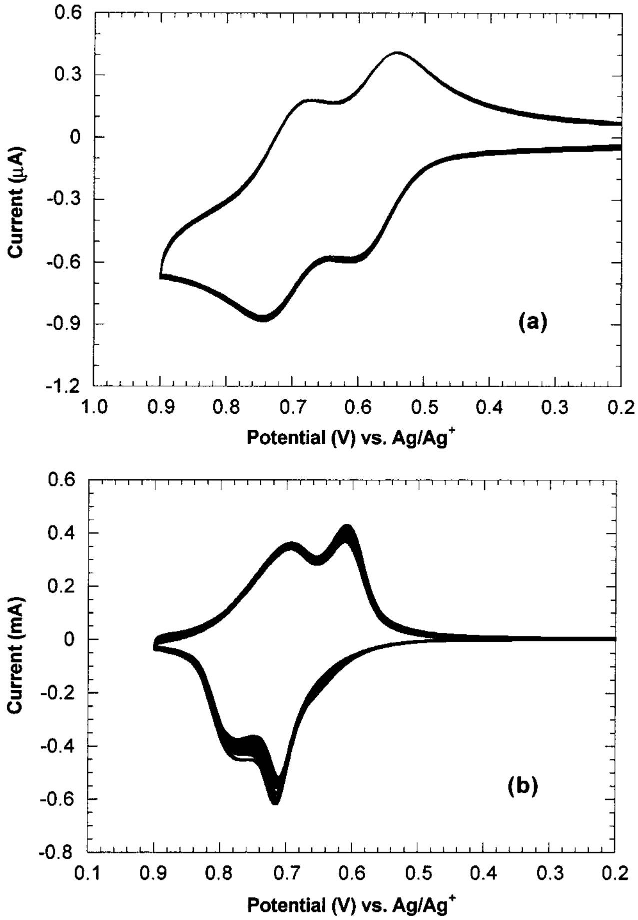


Figure 1. Cyclic voltammograms of (a) TPD in DCE solution and (b) **10** on ITO substrate at a scan rate of 40 mV/s.

properties. The emissive layer consisted of a binaphthyl-containing polyfluorene, P3F1B (the chemical structure is illustrated in Scheme 1),[8] which was spin-cast from its DCE solution (8−15 mg/mL) on the top of HTL with a thickness of 60−100 nm. The sample was then transferred into an argon atmosphere drybox in which the vacuum evaporator was located. A layer of 50 nm thick calcium (Ca) was vacuum-deposited (1 × 10^{-6} Torr) through a mask and was then capped by vacuum deposition of a 80 nm thick silver (Ag) layer to prevent Ca from reacting with moisture and oxygen.

A single-layer device with ITO as the anode, Ca as the cathode, and P3F1B as the emissive layer emitted blue light. The EL spectrum of the P3F1B single-layer device peaked at 420 nm with a turn-on voltage (defined as the voltage from which light can be detected) around 10 V. When the polymer **12** was used as the HTL, the device performance was dramatically improved. The device had a lower turn-on voltage at 6.5 V. The brightness reached 3070 cd/m^2 at a bias voltage of 19.4 V and a current density of 630 mA/cm^2, corresponding to an external quantum efficiency of 0.82% (Figure 2). Compared to the reference single-layer device without **12**, this double-layer device demonstrated more than 3 orders of magnitude of increase in EL quantum efficiency. Although the backbone of these PFCB-containing polymers possessed quite high fluoro content, it did not interfere with the hole-transporting property of the polymer. This could be due to the large size of aromatic triarylamine rings that tend to pack closely; it may facilitate the hole transport on the semi-ladder-type polymer structures. In addition, it may be due to the improvement of morphology on ITO by the PFCB polymer and the balanced charge injection/transport in the double-layer device.

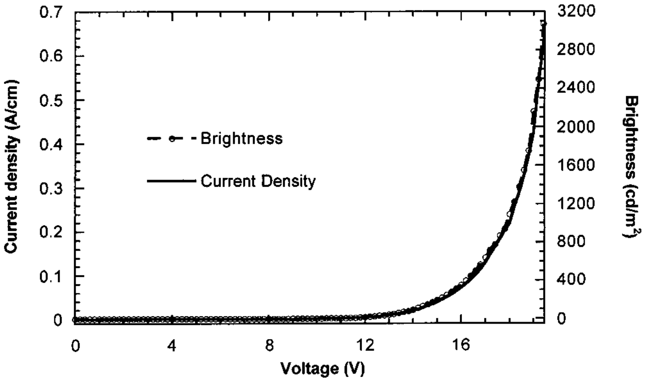


Figure 2. Current density−voltage−brightness characteristics of ITO/di-Bu-TPD-PFCB (**12**)/P3F1B/Ca/Ag device.

In conclusion, we have developed a series of efficient hole-transporting triarylamine-containing polyperfluorocyclobutanes through in-situ thermal polymerization. An efficient blue light-emitting PLED using a fluorene and binaphthyl copolymer as the blue emitter and a TPD-PFCB as the HTL showed a low turn-on voltage (6.5 V), high brightness (3070 cd/m^2), and high external quantum efficiency (0.82%). Further studies on applying this generally applicable approach on both hole transporters and emitters to yield better PLEDs are in progress.

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(8) (a) P3F1B was synthesized via the palladium-catalyzed Suzuki cross-coupling reaction with a molecular weight

(Mw) of 37.1 × 10^3 and polydispersity index of 1.9, as measured by the gel permeation chromatography using THF as the eluent. The ratio between 9,9-dihexylfluorene and 2,2′-dihexyloxy-1,1′-binaphthyl units in the random copolymer was determined by the corresponding aryl-diboronic ester and dibromide at the beginning of the Suzuki reaction.

The band gap of 2.9 eV was extrapolated to its UV absorption band edge. (b) Liu, S.; Jiang, X.; Liu, M. S.; Ma, H.; Jen, A. K.-Y., submitted to *MRS Proc.* (c) Jiang, X.; Liu, S.; Ma, H.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2000**, *76* (14), 1813.

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