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Synthesis and optoelectronic properties of thermally cross-linkable fluorene derivative containing hole-transporting triphenylamine terminals

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ABSTRACT

This paper describes the synthesis of a solution-processable and thermally cross-linkable 2,7-bis-[4-bis(4-vinylphenyl)aminophenyl]-9,9-dihexylfluorene (**VTF**) and its application as hole-transporting layer in multilayer polymer light-emitting diodes (PLEDs). The thermal, photophysical, and electrochemical properties of **VTF** were investigated by differential scanning calorimetry, thermogravimetric analysis, optical spectroscopy, and cyclic voltammetry. The **VTF** is readily cross-linked via vinyl groups by heating at 180 °C for 30 min to obtain homogeneous film with excellent solvent resistance. Multilayer PLEDs (ITO/PEDOT:PSS/cured-**VTF**/MEH-PPV/Ca/Al) were readily fabricated by spin-coating process using cross-linked **VTF** as hole-transporting layer (HTL). The maximum brightness (13,640 cd/m²) and current efficiency (0.69 cd/A) were superior to those without HTL (ITO/PEDOT:PSS/MEH-PPV/Ca/Al: 7810 cd/m², 0.28 cd/A). In addition, the cured-**VTF** could replace conventional hole-injection layer (PEDOT:PSS) to reveal comparable performance (8240 cd/m², 0.44 cd/A). Current results indicate that the **VTF** with four thermally cross-linkable terminal vinyl groups is a promising optoelectronic material, which is readily processed by wet processes.

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1. Introduction

Organic and polymer light-emitting devices (OLEDs and PLEDs) have attracted considerable attention due to their potential applications in solid-state lighting and full-color flat-panel displays [1–6]. The major issues in such applications lie in the feasibility of fabricating large-area devices and the cost of manufacturing technology [7]. Solution processes, such as spin-coating, are believed to be more cost-effective way of fabricating large-area devices. Device performance is another critical factor in determining their potential for applications. To achieve optimum device performance, charges injection and transport from cathode and anode must be balanced to raise the recombination ratio of charges [8]. Multilayer devices are usually fabricated to attain this balance by inserting holetransporting (or injecting) layer (HTL) or electron transporting (or injecting) layer (ETL) in addition to emitting layer [9-14]. For example, Tang and VanSlyke demonstrated efficient multilayer OLEDs using small molecular triphenylamine as HTL and Alg₃ as emitting and electron-transporting layers to balance carriers transport and injection [15]. However, the low molecular weight hole-transporting and emitting materials must be deposited by

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vacuum evaporation, which usually requires strict control of thermal deposition conditions. On the contrary, film formation by solution processes, such as spin-coating and ink-jet printing methods, are relatively easy and cost-effective. Some low molecular weight hole-transporting materials whose films can be obtained by wet processes have been synthesized and applied in OLEDs. For example, Promarak et al. [16] fabricated a multilayer OLED device by wet processes using amorphous fluorene derivative [2,7-bis(4diphenylaminophenyl)-9,9-bis-n-hexylfluorene] as HTL and thermal deposited Alq₃ as emitting layer. The device exhibited bright green emission of 6500 cd/m² and low turn-on voltage of 3.8 V. However, the thermal deposition step eliminated advantages gained by the inherent simplicity of wet processing [17]. Therefore, fabrication of multilayer device by subsequent spin-coating is highly desirable. A major challenge for solution processing is the erosion or dissolution of previously deposited layer by subsequent coating solution.

To avoid this undesirable erosion or dissolution, the utilization of orthogonal solvents for processing has been reported [7,18]. For example, the water soluble poly(styrenesulphonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) has been widely used in OLEDs and PLEDs as a hole-injection layer to enhance the device performance [19]. However, the PEDOT has serious drawbacks such as corrosion of the ITO anode [20,21], poor surface energy match with aromatic emissive layer and exciton quenching at the





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interface between PEDOT and emissive materials [10]. Furthermore, whether PEDOT possesses adequate electron-blocking capacity is another issue needs to be considered [9,22]. To avoid this undesirable erosion or dissolution, cross-linkable precursors with specific functional groups become a necessary for the fabrication of multilayer devices. Several thermally curable triarylamine derivatives containing trifluorovinyl ethers (TFVE) or styryl groups were successfully used as HTLs and demonstrated excellent solvent resistance [8,9,23-25]. Moreover, the optimal HTL should possess not only appropriate HOMO energy level (lying between those of ITO and emitting layer) to facilitate hole-injection but also high electronblocking capacity [22]. However, the cross-linkable HTLs containing trifluorovinyl ether groups (TFVE) required both high curing temperatures (>225 °C) and long curing times (1–2 h). This prolonged high-temperature curing tends to degrade the previously deposited layers. Accordingly, it is highly desirable to develop crosslinkable HTLs which are readily curable at lower temperature (<200 °C). In addition to thermal curing conditions, solvent resistance of the cured film is also an essential requirement for practical applications. For this reason, we attempted to design solutionprocessable and thermally cross-linkable HTLs which can be thermally cured below 200 °C to obtain highly solvent-resistant films.

Previously, we successfully developed thermally cross-linkable poly(fluorene-co-triphenylamine) (PFTV) and solution-processable 4,4',4"-{[9,9-bis(hexyl)-9H-fluorene-2,4,7-triyl]tri-2,1-ethenediyl} tris(N,N-diphenyl) benzeneamine (TF) as hole-transporting materials and obtained good device performances [26,27]. However, some issues left to be solved to enhance device performance further. such as increasing solvent resistance and thermal cross-linking reactivity. Therefore, in this study, we synthesized a new solutionprocessable, thermally cross-linkable 2,7-bis-[4-bis(4-vinylphenyl) aminophenyl]-9,9-dihexylfluorene (VTF) to be applied as holetransporting layer or hole-injection layer. The VTF comprises rigid fluorene as core and hole-transporting triphenylamine as terminals, aiming to retain its thermal and morphological stability and to enhance device performance, respectively [28]. The VTF revealed high thermal cross-linking reactivity (curable below 200 °C within 30 min); its cured film was homogeneous and highly solvent resistant. We find that the VTF integrates thermal cross-linking and hole-transporting ability with high reproducibility in fabricating multilayer PLEDs by successive spin-coating processes. The performance of MEH-PPV device is greatly enhanced by inserting the thermally cured VTF as hole-transporting layer, with the maximum luminance and current efficiency being 13,640 cd/m^2 and 0.69 cd/A, respectively. In addition, the cured-VTF can also be applied as holeinjection layer to replace conventional PEDOT:PSS. The new VTF is a promising hole-transporting material for optoelectronic devices; and more importantly, it can be deposited by spin-coating processes.

2. Materials and methods

2.1. Materials and characterization

4-Bromotriphenylamine (**2**) and 4,4',-(4-bromophenylazanediyl) dibenzaldehyde (**3**) were prepared according to previously reported procedures [29,30].9,9-Dihexylfluorene-2,7-bis(trimethyleneborate), Aliquat 336 and tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄] were purchased from Aldrich Co., Alfa Aesar Co. and Strem Chemicals Inc., respectively. Methanol (ECHO Co.), toluene (Tedia Co.), chloroform (CHCl₃, Tedia Co.) and other solvents were HPLC grade reagents. All reagents and solvents were used without further purification. All newly synthesized compounds were identified by ¹H NMR, ¹³C NMR, and elemental analysis (EA). ¹H NMR and ¹³C NMR spectra were recorded with a Bruker AVANCE-400 NMR spectrometer, with the chemical shifts reported in ppm using tetramethylsilane (TMS) as an

internal standard. The FT-IR spectra were measured as KBr disk using a Fourier transform infrared spectrometer, model 7850 from Jasco. Mass and elemental analysis were carried out on a JEOL JMS-700 spectrometer and Heraus CHN-Rapid elemental analyzer, respectively. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 20 °C/min, using a PerkinElmer TGA-7 thermal analyzer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 1 Star System under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption spectra were measured with a Jasco V-550 spectrophotometer and photoluminescence (PL) spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer. The cyclic voltammograms were recorded using a voltammetric apparatus (model CV-50 W from BAS) at room temperature under nitrogen atmosphere. The measuring cell was composed of an ITO glass as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M $(n-Bu)_4$ NClO₄ as electrolyte. The energy levels were calculated using ferrocene (FOC) as standard (-4.8 eV with respect to vacuum level which is defined as zero) [31,32]. An atomic force microscope (AFM), equipped with a Veeco/Digital Instrument Scanning Probe Microscope (tapping mode) and a Nanoscope IIIa controller, was used to examine surface morphology and to estimate thickness and root-mean-square (rms) roughness of deposited films. The film thickness of hole-transporting and emitting layers were measured by a surface profiler, α -step 500. The static contact angles were measured with water by using a contact angle meter (GBX, PX610. France).

2.2. Synthesis of compound 5 and tetra-functional VTF (Scheme 1)

2.2.1. Synthesis of 2,7-bis-[4,4'-(phenylazanediyl)dibenzaldehyde]-9,9-dihexylfluorene (5)

A mixture of 4,4'-(4-bromophenylazanediyl)dibenzaldehyde (3: 0.8 g, 2.1 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**4**, 0.5 g, 1 mmol), (PPh₃)₄Pd(0) (50 mg, 0.04 mmol) and several drops of Aliguat 336 were added to a mixture consisting of toluene and aqueous solution of K_3PO_4 (2 M). The mixture was first purged with nitrogen and then stirred rigorously at 90 °C for 24 h. The mixture was poured into distilled water after cooling to room temperature and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and vacuum concentrated. The crude product was purified by column chromatography using CHCl₃ as an eluent. The product was re-dissolved in chloroform and poured into a large amount of ethanol; the appearing precipitates were collected by filtration to give yellow solids of 5. The yield was 61% (0.57 g). FT-IR (KBr pellet, cm⁻¹): *v* 3062, 3033, 2931, 2848, 2734, 1691 (-CHO), 1585, 1504, 1467, 1315, 1284, 1213, 1162, 821, 732, 690. ¹H NMR(CD₂Cl₂, ppm): δ 9.93 (s, 4H, –CHO), 7.81–7.83 (d, 10H, Ar–H, J = 8 Hz), 7.72–7.74 (d, 4H, Ar–H, J = 8 Hz), 7.62-7.65 (m, 4H, Ar-H), 7.27-7.31 (m, 12H, Ar-H), 2.07 (s, 4H, -CH₂-), 1.08~1.13 (m, 12H, -CH₂-), 0.75~0.79 (m, 10H, -CH₂- & $-CH_3$). ¹³C NMR (CD₂Cl₂, 400 MHz, ppm): δ 180.54, 142.09, 134.97, 130.44, 129.39, 129.23, 121.71, 121.30, 118.76, 117.37, 116.01, 113.11, 111.47, 110.34, 30.56, 21.68, 19.84, 14.04, 12.73, 3.92. ELEM. ANAL. Calcd. for C₆₅H₆₀N₂O₄ (%): C, 83.66; H, 6.48; N, 3.00. Found: C, 83.65; H, 6.59; N, 2.90. FAB-MS: *m*/*z*: 933 [*M*⁺] (calcd: 932.5).

2.2.2. Synthesis of 2,7-bis-[4-bis(4-vinylphenyl)aminophenyl]-9,9dihexylfluorene (**VTF**)

To a mixture of methyltriphenylphosphonium bromide (1.92 g, 5.36 mmol) in 15 mL of THF was added t-BuOK (5 mL, 5.00 mmol) under cooling and then **5** (0.50 g, 0.535 mmol). The mixture was stirred for 24 h at room temperature, poured into distilled water and extracted with chloroform. The organic layer was dried with



Scheme 1. Synthesis of compound 5 and tetra-functional monomer VTF.

anhydrous magnesium sulfate and vacuum concentrated. The crude product was purified by column chromatography using *n*-hexane/dichloromethane (v/v = 3/1). The product was redissolved in chloroform and poured into a large amount of methanol; the appearing precipitates were collected by filtration to give light yellow solids of VTF. The yield was 58% (0.29 g). FT-IR (KBr pellet, cm⁻¹): v 3083, 3029, 2927, 2856, 1596, 1504, 1461, 1319, 1280, 1180, 1112, 989, 900, 836, 821, 647. ¹H NMR (CDCl₃, ppm): δ 7.73 ~ 7.75 (d, 2H, Ar-H, J = 8 Hz), 7.54 ~ 7.58 (m, 8H, Ar-H), $7.32 \sim 7.34$ (d, 8H, Ar-H, J = 8 Hz), $7.18 \sim 7.20$ (d, 4 H, Ar-H, *J* = 8 Hz), 7.09 ~ 7.11 (d, 8 H, Ar–H, *J* = 8 Hz), 6.65 ~ 6.72 (dd, 4H, Ar-CH = CH₂, J_1 = 17.6 Hz, J_2 = 10.8 Hz), 5.65 ~ 5.69 (d, 4H, $Ar-CH = CH_2$, J = 17.6 Hz), $5.17 \sim 5.20$ (d, 4H, $Ar-CH = CH_2$, $J = 10.8 \text{ Hz}, 2.00 \sim 2.05 \text{ (m, 4H, -CH_2-)}, 1.05 \sim 1.31 \text{ (m, 12H, -CH_2-)}, 0.73 \sim 0.77 \text{ (m, 10H, -CH_2-&-CH_3)}. ^{13}\text{C} \text{ NMR} \text{ (CDCl}_3, 400 \text{ MHz}, 0.13 \text{ MHz},$ ppm): § 151.63, 147.04, 146.50, 139.79, 139.25, 136.16, 132.34, 127.84, 125.55, 124.46, 124.02, 120.90, 119.90, 112.39, 55.21, 40.47, 31.45, 29.69, 23.77, 22.55, 13.97. ELEM. ANAL. Calcd. for C₆₉H₆₈N₂ (%): C, 89.57; H, 7.41; N, 3.03. Found: C, 89.32; H, 7.50; N, 2.96. FAB-MS: m/ *z*: 925 [*M*⁺] (calcd: 924.54).

2.3. Fabrication and characterization of electroluminescent devices

Multilayer light-emitting diodes [ITO/PEDOT:PSS/HTL/MEH-PPV/Ca/Al] or [ITO/HIL/MEH-PPV/Ca/Al] were fabricated to investigate their optoelectronic characteristics. The ITO-coated glass substrate was washed successively in ultrasonic baths of neutral cleaner/de-ionized water (v/v = 1/3) mixture, de-ionized water, acetone and 2-propanol, followed with treatment in a UV-Ozone chamber. A thick hole-injection PEDOT:PSS layer was spin-coated on top of the freshly cleaned ITO glass and annealed at 150 °C for 15 min in a dust-free atmosphere. The hole-transporting layer (HTL) was formed by spin-coating a solution of VTF in toluene (5 mg/mL, 2000 rpm) on top of the PEDOT:PSS layer and thermally treated at 180 °C for 30 min under nitrogen atmosphere. Then the emitting MEH-PPV layer (EML) was spin-coated onto the HTL. The VTF and MEH-PPV solutions were filtered through a syringe filter (0.2 μ m) before the spin-coating. The actual thickness of HTL and EML are about 30 and 100 nm, respectively. Finally, a thick layer of cathode was deposited by successive thermal evaporation of Ca (50 nm) and Al (100 nm) under 110⁻⁶ Torr. The luminance versus bias, current density versus bias, and emission spectra of the PLEDs were recorded using a combination of Keithley power source (model 2400) and Ocean Optics usb2000 fluorescence spectrophotometer. The fabrication of the devices was done in ambient conditions, with the following performance tests conducted in a glove-box filled with nitrogen.

3. Results and discussion

3.1. Synthesis and characterization

Tetra-aldehyde derivative of fluorene (5) was synthesized by the palladium-catalyzed Suzuki coupling of 9,9-dihexylfluorene-2,7bis(trimethyleneborate) (4) and 4,4'-(4-bromophenylazanediyl) dibenzaldehyde (3) as shown in Scheme 1. The target thermally cross-linkable hole-transporting VTF was synthesized by the wellknown Wittig reaction from 5 and methyltriphenylphosphonium bromide. Chemical structure of 5 and target tetra-functional VTF were satisfactorily confirmed by ¹H NMR, ¹³C NMR spectra, elemental analysis, and mass spectrometry. Fig. S1 (Supporting Information) shows the ¹H NMR spectra of **5**, in which the characteristic chemical shift at 9.93 ppm is assigned to protons of the aldehyde substituents (-CHO). And as shown in Fig. 1, the characteristic peak at 9.93 ppm disappears completely in ¹H NMR spectra of tetra-functional VTF, with new proton peaks appearing obviously at $6.65 \sim 6.72$ and 5.17 ~ 5.69 ppm attributable to vinyl substituents (=CH- and = CH_2). The proton's absorption peaks was assigned according to the HMBC



Fig. 1. ¹H NMR spectrum of **VTF** in CDCl₃.

(Heteronuclear Multiple Bond Coherence) spectrum of **VTF** [Fig. S1(b)]. Successful synthesis of 2,7-bis-[4-bis(4-vinylphenyl) aminophenyl]-9,9-bis-n-hexylfluorene (**VTF**) was ascertained from the 1:1 area ratio of peak a (=CH₂ in vinyl) over peak i (-CH₂ in alkyl chain of fluorene). The characteristic chemical peaks at 6.65 ~ 6.72 and 5.17 ~ 5.69 ppm confirms the existence of vinyl groups, from which thermally cross-linkable character can be expected. In combination with the data of mass and elemental analysis, the successful synthesis of **VTF** has been confirmed. The **VTF** is soluble in common organic solvents such as chloroform, THF, toluene, and chlorobenzene.

3.2. Thermal cross-linking properties and surface morphology of **VTF**

Since **VTF** contains reactive vinyl groups which will give rise to networks structure (cross-linking) under proper thermal treatment. Thermal cross-linking and thermal resistant characteristics of VTF were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively (Table 1). The thermal decomposition temperature (T_d , 5% weight loss) of **VTF** is 512 °C under nitrogen atmosphere, indicating that the VTF is highly thermal stable (Fig. S2). As shown in Fig. 2, during the first heating scan the DSC trace of VTF shows an exothermic peak at 184 °C, in which the exotherm starts at about 175 °C. The heat released (86.1 J/g) is attributed to cross-linking reaction of the periphery vinyl groups. However, no obvious exotherm is observed in the second heating scan, indicating the cross-linking has been completed during the first scan. Furthermore, the glass-transition temperature (T_g) of the cured **VTF** is about 198 °C with no detectable crystallization and melting transition, suggesting that it is basically an amorphous material (as shown in inset). The high T_g is highly desirable to prevent the crystallization process, during device operation or thermal annealing, which deteriorates longterm morphological stability. The reaction time required to cure VTF was estimated using isothermal DSC technique. The exothermic thermal cross-linking of VTF under 180 °C is completed within 30 min (Fig. S3). This can be confirmed by the absence of exothermic peak in the DSC trace of the cross-linked sample. To ensure complete cross-linking in the following study, the crosslinking of all VTF films was conducted at 180 °C for 30 min under nitrogen atmosphere. Moreover, the cross-linking behaviors of the VTF film were investigated by FT-IR spectra (Fig. S4). The peaks around 900 and 987 cm⁻¹ corresponding to the vinyl C–H out-ofplane deformation vibration and 1625 cm⁻¹ corresponding to the vinyl C=C stretching vibration decreased significantly after the thermal curing. The cured films became insoluble in solvents. These results indicate that the cross-linking of vinyl groups has been completed under these conditions.

Low molecular weight hole-transporting materials, such as N,N'-di-[(1- naphthalenyl)-N,N'-diphenyl]-(1,1'-biphenyl)-4,4'- diamine (NPB), are widely used in the fabrication of OLEDs.

Table 1	
Thermal and Electrochemical Properties of VTF.	

	T _g	<i>T</i> _d	E _{ox} vs. FOC	E _{HOMO}	E _{LUMO}	Eg ^{opt}
	(°C) ^a	(°C) ^b	(V) ^c	(eV) ^d	(eV) ^e	(eV) ^f
VTF	198	512	0.49	-5.29	-2.39	2.90

^a Determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.

^b The temperature at 5 wt% loss in nitrogen atmosphere, measured by TGA.

 $^{\rm c}$ $E_{\rm FOC} = 0.48$ V vs. Ag/AgCl.

^d $E_{\text{HOMO}} = -(E_{\text{ox, FOC}} + 4.8) \text{ eV}.$

 $E_{LUMO} = E_g + E_{HOMO}$

^f Band gaps obtained from onset absorption (λ_{onset}): $E_g = 1240/\lambda_{onset}$.



Fig. 2. DSC traces of VTF at a heating rate of 10 $^\circ$ C/min. The first scan was used to observe the reaction heat of vinyl groups.

However, NPB layer must be deposited by thermal evaporation under vacuum due to its poor film-forming property obtainable in solution processes such as spin-coating. Homogeneous film is a prerequisite to fabricate OLEDs and PLEDs with high device performance and long lifetime. Furthermore, to achieve efficient emission in PLEDs, it is imperative to obtain highly homogeneous film for each layer. The morphology of VTF film obtained by spincoating on ITO substrate, before and after thermal curing, was investigated using atomic force microscope (AFM: tapping mode). As shown in Fig. 3, the surface morphology of VTF film before thermal curing is quite homogeneous, with the root-mean-square (rms) roughness being 1.63 nm. However, the film homogeneity is further improved after the thermal curing at 180 °C, 30 min. The cured film is pinhole- and aggregate-free, with the rms roughness being reduced to 1.24 nm. This homogeneous surface morphology of VTF after thermal cross-linking is beneficial for obtaining high performance PLED devices.

3.3. Optical and electrochemical properties

Fabrication of multilayer PLEDs by solution processes absolutely requires that previously deposited layer should be resistant to the subsequent coating solutions. To examine solvent resistance of the **VTF** films before and after thermal curing (180 °C, 30 min), they were spin-coated with chlorobenzene (good solvent of **VTF**) to evaluate their dissolution behaviors. As shown in Fig. 4, the absorption spectrum of pristine **VTF** film disappears almost completely after the spin-coating, meaning that the **VTF** film is dissolved by chlorobenzene during the coating process. However, the absorption spectrum of thermal cured-**VTF** film remains almost unchanged after the spin-coating. This indicates that cured-**VTF** is highly solvent-resistant, which is attributed to its highly crosslinked structure after the thermal curing. This characteristic makes **VTF** suitable for the fabrication of multilayer PLEDs by solution processes.

Cyclic voltammetry (CV) is an effective method in investigating reduction-oxidation behaviors of thin films insoluble in electrolyte solution [33,34]. Because the **VTF** is readily formed as homogeneous film that is insoluble in acetonitrile, it was deposited on an ITO glass to be applied as the working electrode. The electrode was supported in anhydrous acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate [(n-Bu)₄NClO₄] for CV measurements. The highest occupied molecular orbital (HOMO) which corresponds to ionization potential (IP) can be estimated from the onset oxidation



Fig. 3. The AFM images of VTF films coated on ITO glass: (a) pristine film, rms roughness = 1.63 nm; (b) film thermally treated at 180 °C for 30 min, rms roughness = 1.24 nm.

potential (E_{ox}) revealed in CV by the equation $E_{HOMO} = -(E_{ox} + 4.8)$ eV. Fig. S4 shows the cyclic voltammograms of the cured-**VTF** film (180 °C for 30 min), the onset oxidation potential is observed at 0.49 V (versus ferrocene) and the HOMO level estimated to be -5.29 eV. The lowest unoccupied molecular orbital (LUMO) level is estimated to be -2.39 eV, using the HOMO level and the optical band gap (E_g) calculated from onset absorption (Table 1). Fig. 5 illustrates the energy levels of cured-**VTF**, PEDOT:PSS and work functions of electrodes. Clearly, the HOMO level of cured-**VTF** (-5.29 eV) is close to that of ITO/PEDOT:PSS (-5.2 eV) and the barrier height (ΔE_h) for hole injection between PEDOT:PSS and **VTF** is 0.09 eV, facilitating the injection and transport of holes. Accordingly, the cured-**VTF** is a potential hole-injection and transporting material.



Fig. 4. Absorption spectra of pristine and cured-**VTF** films: (-) before and (-) after spin-coated with pure chlorobenzene. The cross-linking was conducted at 180 °C for 30 min under nitrogen atmosphere.

3.4. Optoelectronic properties of multilayer PLEDs using **VTF** as hole-transport layer

To evaluate the applicability of the cured-VTF as holetransporting layer, multilayer polymer light-emitting diode, with a device configuration of [ITO/PEDOT:PSS/cured-VTF/MEH-PPV/ Ca(50 nm)/Al(100 nm)], was investigated by successive spincoating process to investigate their optoelectronic properties. The device without cured-VTF as hole-transporting layer (ITO/ PEDOT:PSS/MEH-PPV/Ca/Al) was also fabricated simultaneously for comparative study. The transparent and insoluble cured-VTF film was fabricated by spin-coating VTF solution on top of the PEDOT:PSS layer and then curing at 180 °C for 30 min under nitrogen atmosphere. The current density versus bias and brightness versus bias curves (I-B-V) of the electroluminescent (EL) devices are shown in Fig. 6, with the corresponding characteristic data summarized in Table 2. Fig. 7 shows the electroluminescent spectra of PLED using cured-VTF as hole-transporting layer (HTL), the main emission peaks are situated around 584 and 622 nm. Its EL spectrum is analogous to that of device without VTL layer, suggesting that the emission is originated from emitting MEH-PPV layer. Furthermore, inserting a cured-VTF as HTL significantly improves device performance, i.e., the maximum brightness and maximum current efficiency are enhanced from 7810 cd/m² and 0.28 cd/A (without HTL) to 13,640 cd/m² and 0.69 cd/A, respectively. The turn-on voltage is increased from 3.1 V to 4.1 V when the cured-VTF is inserted as HTL (Fig. 6 & Table 2). Inserting a cured-**VTF** layer reduces the current density at lower voltage (<6.5 V), which is probably caused by the retarded hole-injection due to its



Fig. 5. The energy level diagrams of cured-VTF, PEDOT:PSS and electrodes.



Fig. 6. Current density versus bias and brightness versus bias characteristics of the polymer light-emitting diodes. Device structure: (-) ITO/PEDOT:PSS/MEH-PPV/Ca/Al; -) ITO/PEDOT:PSS/cured-VTF/MEH-PPV/Ca/Al; (-**-) ITO/cured-VTF/MEH-PPV/ Ca/Al; HIL: hole-injection layer, HTL: hole-transporting layer.

lower HOMO level (-5.29 eV) than that of MEH-PPV (-5.02 eV). Higher voltages raise the current density quickly owing to the fact that many holes gain enough energy to conquer the barrier height. The responses of the current efficiency to the operating voltage are depicted in Fig. S6. Inserting cured-VTF as hole-transporting layer raises the device current efficiency for about two times. The performance enhancement is attributable to more balanced charges injection and transport in the MEH-PPV layer due to the presence of the cured-VTF as hole-transporting layer. As mentioned above, the HOMO level of cured-VTF (-5.29 eV) is close to that of PEDOT:PSS (-5.2 eV) to facilitate hole injection and transport. Additionally, the cured-VTF also acts as electron-blocking layer because of its high LUMO level (-2.39 eV, Fig. 5). Therefore, the cured-VTF layer not only effectively confines the excitons in MEH-PPV layer but also prevents the PEDOT:PSS chain from penetrating into the MEH-PPV layer to quench the emission [9,25,35].

Table 2			
Optoelectronic Properties	s of the	Multilayer	PLEDs. ^a

HIL/HTL	$V_{on}\left(V\right)^{b}$	$L_{max} (cd/m^2)^c$	$LE_{max}(cd/A)^d$	CIE 1931 (x, y) ^e
PEDOT(HIL)	3.1	7810	0.28	(0.58, 0.42)
PEDOT(HIL)/	4.1	13,640	0.69	(0.58, 0.42)
cured-VTF(HTL)				
cured-VTF(HIL)	4.6	8240	0.44	(0.58, 0.42)

^a Device structure: ITO/HIL/HTL/MEH-PPV/Ca/Al; HIL: hole-injection layer, HTL: hole-transporting layer.

Turn-on voltage defined as the bias at a luminance of 10 cd/m^2 .

^c Maximum luminance. ^d Maximum luminance efficiency.

^e The 1931 CIE coordinates at *ca*. 1000 cd/m².



Fig. 7. Electroluminescent spectra of polymer light-emitting diodes. Device structure: (-) ITO/PEDOT:PSS/MEH-PPV/Ca/Al; (--) ITO/PEDOT:PSS/cured-VTF/MEH-PPV/Ca/Al; (-••-)ITO/cured-VTF/MEH-PPV/Ca/Al; HIL: hole-injection layer, HTL: holetransporting layer.

Moreover, a PLED with cured-VTF as hole-injection layer (HIL) [ITO/cured-VTF/MEH-PPV/Ca/Al] was also fabricated to evaluate the applicability of **VTF** as HIL. The turn-on voltage (at 10 cd/m^2) is increased from 3.1 V to 4.6 V when the PEDO:PSS is replaced with cured-VTF as HIL (Table 2). This indicates that cured-VTF layer raises the barrier height for hole injection when compared to PEDOT:PSS layer. The aqueous contact angle of ITO substrate, ITO/ PEDOT:PSS and cured-**VTF** are $<5^{\circ}$, 10–20° and 78°, respectively. The surface energy mismatch between hydrophilic ITO and hydrophobic cured-VTF is likely to cause poor physical-electronic contact at the ITO/cured-VTF interface [22]. However, its maximum brightness (8240 cd/m²) and maximum current efficiency (0.44 cd/A) are still superior to those with PEDOT:PSS as HIL $(7810 \text{ cd/m}^2, 0.28 \text{ cd/A})$. This suggests that the cured-**VTF** acts as buffer layer with electron-blocking feature that results in more balanced hole and electron fluxes [22,23]. To conclude, the cured-**VTF** is a promising hole-transporting and hole-injection material for the fabrication of efficient multilayer PLEDs by successive spincoating processes.

4. Conclusions

We have successfully prepared a hole-transporting 2,7-bis-[4bis(4-vinylphenyl)aminophenyl]-9,9-dihexylfluorene (VTF) containing thermally reactive vinyl groups by the Wittig reaction. The VTF demonstrated high thermal stability with thermal decomposition (T_d) being 512 °C and exothermic peaks at 184 °C due to thermal cross-linking of the vinvl groups. The glass-transition temperature was 198 °C after thermal curing at 180 °C for 30 min. The cured-VTF was highly solvent-resistant, attributed to its highly cross-linked structure after the thermal curing. Moreover, the thermal curing resulted in homogeneous surface morphology, with the root-mean-square roughness being 1.24 nm. Multilayer devices using cured-VTF as hole-transporting layer [ITO/ PEDOT:PSS/cured-VTF/MEH-PPV/Ca/Al] were readily fabricated by successive spin-coating processes. The device performance was significantly enhanced, by using the cured-VTF as holetransporting layer. The optimal maximum luminance and maximum current efficiency were 13,640 cd/m² and 0.69 cd/A, respectively, which were superior to those without cured-VTF as hole-transporting layer (7810 cd/m², 0.28 cd/A). Moreover, the cured-VTF was also used as hole-injection layer, instead of conventional PEDOT:PSS, to obtain comparable device performance

 $(8240 \text{ cd/m}^2, 0.44 \text{ cd/A})$. Current results reveal that the thermally cross-linkable **VTF** is a promising hole-transporting and hole-injection material, applicable for the fabrication of multilayer PLEDs by successive wet processes.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.05.036.

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