

Crosslinkable triphenylamine-based hole-transporting polymers for solution-processed polymer light-emitting diodes



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ABSTRACT

We report the synthesis and characterization of a thermally crosslinkable hole-transporting poly(indenofluorene-co-triphenylamine) copolymer (X-IFTP) containing a vinyl-functionalized triphenylamine moiety. This copolymer exhibited an exothermal peak at 125 °C in the first heating/cooling cycle of a differential scanning calorimetry study, indicating that crosslinking occurred. The highest occupied molecular orbital energy level of this copolymer was estimated to be -5.30 eV, as determined by cyclic voltammetry measurement. Flat and uniform films were formed by spin casting X-IFTP from chlorobenzene solution. Crosslinking can be finished by thermally annealing the film at 150 °C for 24 min, which can be confirmed by reflectance Fourier transform infrared spectroscopy and UV–Vis absorption spectra. Multi-layer polymer light-emitting diodes (PLEDs) incorporating X-IFTP as the hole transport layer and a green-light-emitting copolymer as the emissive layer exhibited enhanced luminous efficiency relative to that of a control device without a hole transport layer. Thus, the developed cross-linkable copolymer X-IFTP is a promising material for the construction of efficient PLEDs.

1. Introduction

Over the past two decades, remarkable progress has been made in the development of polymer lighting-emitting diodes (PLEDs) [1–8]. Potential applications of PLEDs include large-area flat panel displays and solid-state lighting. However, current PLEDs typically exhibit unbalanced charge carrier injection and transportation, which results in low efficiency and poor stability [9–15]. To increase the efficiency of PLEDs, a range of functional layers, such as the hole transport layer (HTL), emissive layer, and electron transport layer (ETL), are required to facilitate charge carrier injection and transportation, to enhance the recombination of electrons and holes, and significantly improve electroluminescent performance [16–21]. The HTL is critical in solution-processed PLEDs, and typically requires a solution-processed material that can either be solidified or processed by an orthogonal solvent system. However, this requirement hinders device fabrication because the prefabricated layer can be easily washed away or corroded during the solution processing of a successive layer, as damage to the HTL is detrimental to the optoelectronic properties of the resulting device [22–25].

Various strategies have been developed to overcome interfacial

mixing between layers; for instance, utilizing orthogonal solvents [26], and developing materials composed of thermally removable moieties [27,28] or crosslinkable functional groups [29–32] that can be solidified after processing. Previous studies have shown that combining $N^4,N^{4'}$ -bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)- $N^4,N^{4'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine and $N^4,N^{4'}$ -bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)oxy)phenyl)- $N^4,N^{4'}$ -bis(4-methoxyphenyl)-[1,1'-biphenyl]-4,4'-diamine with a four-member ether ring onto a N,N' -diphenyl- N,N' -(bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine side chain dramatically increased luminous efficiency from 20 to 67 cd A^{-1} [33]. The crosslinkable HTL facilitates hole injection and can restrain electron shift in the HTL and light-emitting layer interface. Moreover, it has been shown that processing (phosphazene-9-yl)carbazole containing 1,2-dihydrocyclobutabenzen under high-temperature curing conditions for a short period of time resulted in a green phosphorescent OLED device with a high luminous efficiency of 48 cd A^{-1} [34]. However, most of these materials require high temperatures to induce crosslinking or are unstable in air [35,36]. Although many solution-processable hole-transporting materials have been synthesized, it is necessary to develop novel crosslinkable polymers to form robust films.

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In the present study, we developed a novel hole-transport polymer by incorporating a vinyl group into a triphenylamine (TPA) unit to realize a crosslinkable HTL material. TPA has been extensively used as a hole transport species to reduce the hole injection barrier because of its suitable appropriate highest occupied molecular orbital (HOMO) energy levels (E_{HOMO}) and excellent hole transport properties [37–39]. For example, the TPA-based high-mobility hole transport copolymer poly(9,9'-dioctylfluorene-co-*N*-(4-butylphenyl)diphenylamine) (TFB) can form smooth and insoluble layers a few nanometers thick, that are robust to solvent rinsing, via thermal treatment at 180–200 °C [40,41]. The incorporation of a TFB layer between PEDOT:PSS and poly(9,9'-dioctylfluorene)-co-(benzothiadiazole) (PFO-BT8, containing 8 mol% BT) can effectively prevent quenching of radiative excitons at the PEDOT:PSS interface [42].

The copolymer (X-IFTPA) developed in the present study has similar E_{HOMO} and lowest unoccupied molecular orbital (LUMO) energy levels (E_{LUMO}) to those of TFB. The cross-linked films formed after thermal treatment exhibited excellent solvent resistance properties. The replacement of the fluorene moiety in the main polymer chain with an indeno-fluorene moiety resulted in higher photoluminescence quantum efficiency (PLQY) [43,44]. Moreover, the incorporated vinyl group will not generate unexpected moieties that are detrimental to the light-emitting performance of devices incorporating this novel polymer.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 shows the synthesis routes for the target copolymers. All of the copolymers were synthesized via palladium-catalyzed Suzuki polymerization of the diboronic ester monomer 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**M1**) with a dibromo monomer: 2,7-dibromo-9,9-dioctyl-9H-fluorene (**M2**), 2,8-dibromo-6,6,12,12-tetraoctyl-6,12-dihydroindeno[1,2-*b*]fluorene (**M3**), or 4-bromo-*N*-(4-bromophenyl)-*N*-(4-vinylphenyl)aniline (**M4**). The reaction of **M1** with **M2**, **M3**, and **M4** yielded the target copolymers TFB, IFTPA, and X-IFTPA, respectively. The molecular structures of these copolymers were confirmed by proton nuclear magnetic resonance (^1H NMR) spectra (see Fig. S1 in the SI). The copolymers were purified by Soxhlet extraction via successive elution with methanol, acetone, and tetrahydrofuran (THF). The copolymers were reprecipitated from THF with methanol. The number average molecular weight (M_n) of the copolymers was measured by gel permeation chromatography (GPC) using THF as the eluent and linear polystyrene as

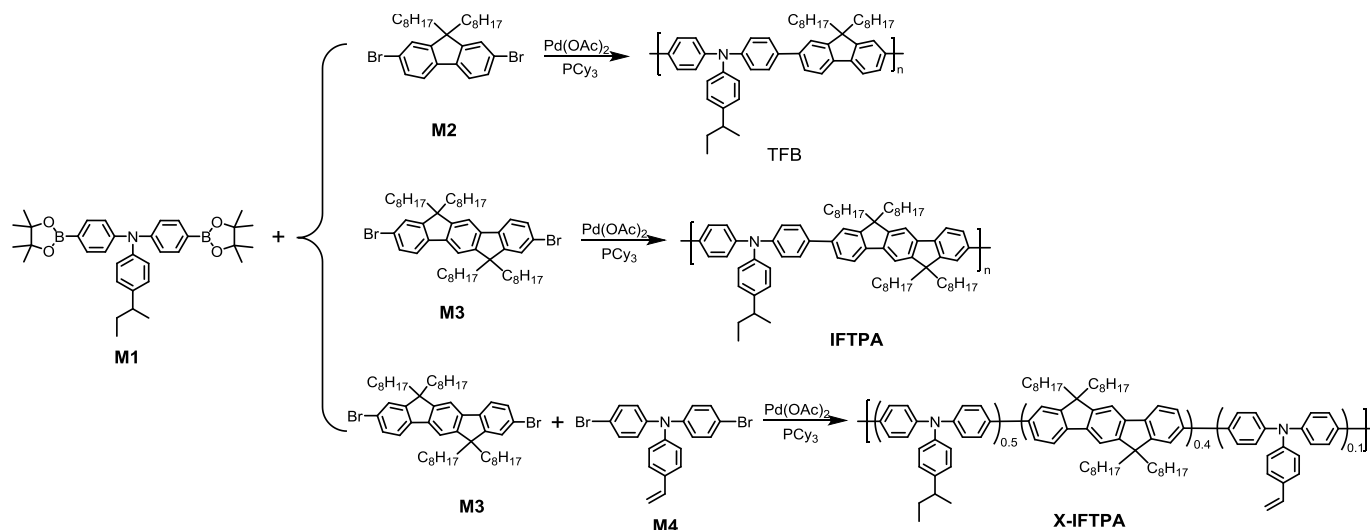
the standard. The M_n values and polydispersity indexes of TFB, IFTPA, and X-IFTPA were estimated to be 32.4, 15.6, and 15.0 kDa and 1.88, 1.88, and 2.68, respectively.

2.2. Thermal properties

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to evaluate the thermal properties of TFB, IFTPA, and X-IFTPA, with relevant characteristics shown in Fig. 1 and Fig. S2 (see in the SI), respectively. No discernible thermal transitions were observed for TFB or IFTPA in the first and second heating/cooling (20 °C min⁻¹) cycles from 30 to 250 °C in nitrogen (Fig. 1a and b). In contrast, an exothermic peak was observed at 125 °C in the first heating/cooling cycle of X-IFTPA (Fig. 1c). This peak suggests the occurrence of a crosslinking reaction of the vinyl groups attached in the TPA moiety. This peak was not observed in the second heating/cooling cycle, which indicates that crosslinking was completed during the first cycle. The thermal decomposition temperatures (defined as 5% weight loss temperature, T_d) of copolymers were higher than 400 °C, as evaluated from TGA characteristics, which indicated the copolymers have a good thermal stability when thermally annealed at relatively low temperature.

2.3. Optical properties

Normalized UV–Vis absorption and photoluminescence (PL) spectra of TFB, IFTPA, and X-IFTPA thin films are shown in Fig. 2. The maximum UV–Vis absorption peaks of IFTPA and X-IFTPA are located at 388 nm, and are slightly red-shifted relative to the maximum absorption of TFB (383 nm) because of the greater conjugation length of the indole-fluorene moiety (Fig. 2a). In the PL spectra (Fig. 2b), the maximum emission peaks of IFTPA and X-IFTPA occur at 453 and 462 nm, respectively. These peaks are significantly red-shifted relative to the maximum PL of TFB (428 nm). Moreover, from Fig. 2b one can clearly observe that the shoulder emission peaks emerged at low-energy region located at about 483 and 487 nm for IFTPA and X-IFTPA, respectively, which might be attributable to the intramolecular interactions between the indenofluorene (with enlarged planarity) and the TPA derivative moiety. In addition, the UV–Vis absorption and PL spectra of X-IFTPA were red-shifted relative to those of IFTPA. This was attributed to the higher molar ratio of triphenylamine units in the polymer backbone of X-IFTPA [45,46]. From the onset of the absorption profiles, the optical band gaps (E_g^{opt}) of TFB, IFTPA, and X-IFTPA were calculated to be 2.88, 2.84, and 2.82 eV, respectively. Detailed photophysical



Scheme 1. Synthetic routes for TFB, IFTPA, and X-IFTPA.

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