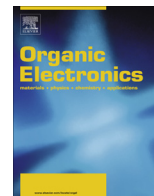




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Using *d*-limonene as the non-aromatic and non-chlorinated solvent for the fabrications of high performance polymer light-emitting diodes and field-effect transistors

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ABSTRACT

Aiming to environment protection, green solvents are crucial for commercialization of solution-processed optoelectronic devices. In this work, *d*-limonene, a natural product, was introduced as the non-aromatic and non-chlorinated solvent for processing of polymer light-emitting diodes (PLEDs) and organic field effect transistors (OFETs). It was found that *d*-limonene could be a good solvent for a blue-emitting polyfluorene-based random copolymer for PLEDs and an alternating copolymer FBT-Th₄(1,4) with high hole mobility (μ_h) for OFETs. In comparisons to routine solvent-casted films of the two conjugated polymers, the resulting *d*-limonene-deposited films could show comparable film qualities, based on UV–vis absorption spectra and observations by atomic force microscopy (AFM). With *d*-limonene as the processing solvent, efficient blue PLEDs with CIE coordinates of (0.16, 0.16), maximum external quantum efficiency of 3.57%, and luminous efficiency of 3.66 cd/A, and OFETs with outstanding μ_h of 1.06 cm² (V s)⁻¹ were demonstrated. Our results suggest that *d*-limonene would be a promising non-aromatic and non-chlorinated solvent for solution processing of conjugated polymers and molecules for optoelectronic device applications.

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1. Introduction

In the past two decades, organic optoelectronic devices, such as organic light-emitting diodes (OLEDs) [1,2], organic field-effect transistors (OFETs) [3,4], and organic photovoltaic cells (OPVs) [5–9], have attracted great attentions. Organic semiconductors for the active layers of the organic devices can be fabricated by vacuum depositions of small molecules or solution depositions for polymers and larger molecules. In the solution processing, a solvent is needed to dissolve an organic material, and then its thin solid film can be deposited typically by spin-coating, screen printing [10], and blade-coating [11]. In comparison to vacuum technology, the solution processing is relatively convenient to fabricate a thin solid film. Moreover, the solution processing has big potential to supply a large area and low cost film, from which polymer optoelectronic devices based on conjugated polymers have received wide interest from scientific communities.

Normally, a conjugated polymer, based on aromatic units, possesses a rigid backbone. In order to dissolve conjugated polymers,

toluene, *p*-xylene, chloroform, chlorobenzene (CB), *o*-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene, are the common solvents. In general, the toluene and *p*-xylene have been widely utilized for the solution-processing of polymer light-emitting diodes (PLEDs) while the CB and DCB are typically applied for solution-processed OFETs and OPVs. However, these aromatic and/or chlorinated solvents are toxic and hazardous to human health and environment [12]. In many countries, more and more strict policies have been established to protect the environment and human health. Therefore, using non-aromatic and non-chlorinated solvents for the solution processing of optoelectronic devices based on conjugated polymers would be highly desirable, especially for commercial purpose.

For the fabrications of OPVs, using *o*-xylene [13,14], trimethylbenzene (TMB) [15–17], *N*-methyl-2-pyrrolidone (NMP) [18], and benzaldehyde [19] as the processing solvents to replace the highly toxic CB or DCB have been reported, among which the *o*-xylene, TMB, and benzaldehyde are still aromatic. There are relatively rare reports on selections of non-aromatic and non-chlorinated solvents for polymer-based OLEDs and OFETs. In a recent report by Liu et al. [20], *n*-butanol and isopropanol were selected as the processing solvents for phosphorescent OLEDs based on iridium(III)

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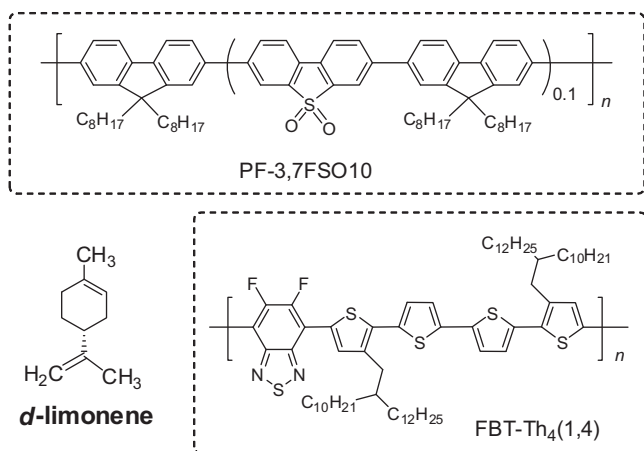


Fig. 1. The molecular structures of *d*-limonene, PF-3,7FSO10, and FBT-Th₄(1,4). The PF-3,7FSO10 is a blue-emissive polymer for polymer light-emitting diodes. The FBT-Th₄(1,4) is a polymer for OFETs.

complex and small molecular hosts, where higher device performances than CB-processed OLEDs were achieved. In a report by Heaney and coworkers [21], a 1:1 mixture of TMB and 1-methylnaphthalene as the non-chlorinated solvent was introduced to fabricate polymer-based OFETs, where a high hole mobility (μ_{th}) of $0.26 \text{ cm}^2 (\text{V s})^{-1}$ was demonstrated.

It is of interest to find new non-aromatic and non-chlorinated solvents for highly efficient optoelectronic devices. In this work, *d*-limonene (Fig. 1) was utilized as a non-aromatic and non-chlorinated solvent for the fabrications of high performance polymer-based OLEDs and OFETs. Limonene is a colorless liquid with a citrus odor. The chemical exists as two optical isomers, *d*-limonene (found in oranges) and *l*-limonene (present in lemons), and the racemic mixture dipentene (*dl*-limonene) [22]. The predominant isomeric form of limonene is *d*-limonene, which is present in nearly 98% of all citrus oils [22]. The world production of *d*-limonene is over 70,000 tons per year [23], supplying with low price. *d*-Limonene is considered to be a natural substance possessing low toxicity (oral LD 50 values 5–6 g/kg) [24] and registered in the Code of Federal Regulation (CFR) [25] as a generally recognized as safe (GRAS) substance for synthetic flavorings. Currently, *d*-limonene is widely used as a flavor and fragrance additive in perfumes, soaps, foods, chewing gum, and beverages [22]. During storage under dark, *d*-limonene can be fairly stable. However, *d*-limonene can be biodegradable in soil or be photochemically decomposed in humid air under sunlight [26]. The boiling point for *d*-limonene is $176 \text{ }^\circ\text{C}$, very close to $180 \text{ }^\circ\text{C}$ for DCB. Delightedly, we found *d*-limonene could show good solubility to dissolve several kinds of conjugated polymers. For example, a random copolymer PF-3,7FSO10 containing fluorene and dibenzothiothiophene-5,5-dioxide [27] and an alternating copolymer FBT-Th₄(1,4) based on difluorobenzothiadiazole and quarterthiophene [28] could be well dissolved in *d*-limonene. The chemical structures of the two conjugated polymers are also shown in Fig. 1. The blue-emissive PF-3,7FSO10 with a high photoluminescence (PL) quantum yield of 74% [27] was utilized to fabricate blue PLEDs. FBT-Th₄(1,4), already shown a high hole mobility [28], was selected for OFETs. Device performances were compared based on active layers spin-coated with solutions of *d*-limonene and corresponding routine solvents already utilized in previous reports. A low toxic solvent may allow the solution processing to be conducted directly in air, which is very convenient and highly valuable for industry application. Thus we also performed fabrications of active layers with *d*-limonene solutions in air. With *d*-limonene as the solvent for PF-3,7FSO10, high performed blue PLEDs with

CIE coordinates of (0.16, 0.16), maximum external quantum efficiency (EQE_{max}) of 3.57%, and luminous efficiency (LE_{max}) of 3.66 cd/A were demonstrated. The device efficiencies were even slightly higher than those of devices fabricated with *p*-xylene. The FBT-Th₄(1,4) based OFETs fabricated with *d*-limonene showed an outstanding μ_{th} of $1.06 \text{ cm}^2 (\text{V s})^{-1}$. Under the same experimental condition, the OFET with DCB as the processing solvent exhibited a μ_{th} of $1.00 \text{ cm}^2 (\text{V s})^{-1}$. Encouragingly, almost comparable device performances were achieved when the two kinds of *d*-limonene-processed devices were fabricated in air, implying very limited air interference. Our results suggest that *d*-limonene, a natural product, is a promising non-aromatic and non-chlorinated solvent for solution processing of conjugated polymers and molecules for optoelectronic device applications.

2. Experimental

2.1. Materials

The synthesis of PF-3,7FSO10 and FBT-Th₄(1,4) had been reported elsewhere [27,28]. *p*-Xylene, chlorobenzene, *o*-dichlorobenzene, and *d*-limonene were purchased from Aldrich. *d*-Limonene was purified by passing through a short silica-gel column before use.

2.2. Fabrication and characterization of polymer light-emitting diodes

Patterned indium tin oxide (ITO) coated glass with a sheet resistance of $<17 \text{ ohm/square}$ were cleaned inside an ultrasonic bath, beginning with acetone, followed by surfactant scrub, deionized water and isopropanol. After oxygen plasma cleaning for 5 min, a 40 nm-thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios AL4083 from Heraeus) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in a vacuum oven at $120 \text{ }^\circ\text{C}$ for 20 min. The PF-3,7FSO10 solutions in *p*-xylene or *d*-limonene were prepared by stirring at $40 \text{ }^\circ\text{C}$ for overnight. The polymer solutions were spin-coated onto PEDOT:PSS films inside a N_2 filled glove box or in ambient air. Then 1.5 nm thickness of CsF and 100 nm Al electrode were evaporated through a shadow mask of 0.165 cm^2 . The current density–luminance–voltage (J – L – V) characteristics were measured in the N_2 filled glove box using a Keithley 236 source-measurement unit and a calibrated silicon photodiode. The CIE color coordinates and electroluminescence spectra were recorded using PR-705 SpectraScan spectrophotometer (Photo Research).

2.3. Fabrication and characterization of OFETs

To measure the hole mobilities of the polymer, OFETs were fabricated in a top contact geometry using silver as the source and drain electrode. Highly *n*-doped silicon and thermally grown silicon dioxide (300 nm) were used as the back gate and gate dielectric, respectively. Octyltrichlorosilane (OTS) was then used for surface modification of the gate dielectric layer. The copolymer film (60 nm) was spin-coated on OTS treated substrates from a dichlorobenzene solution. Then silver film (60 nm) was deposited under vacuum as the source and drain electrodes. The width to length ratio (W/L) of the FET devices is 60/1. All the OFETs were annealed at $100 \text{ }^\circ\text{C}$ in air. The OFETs characterizations were performed in air by using a probe station and a semiconductor parameter analyzer (Agilent 4155C). Then field-effect mobility was calculated from the standard equation for saturation region in metal–dioxide–semiconductor field effect transistors: $I_{\text{DS}} = (W/2L)\mu_{\text{C}}(V_{\text{G}} - V_{\text{th}})^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W and L are the channel width and

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