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# Electron-Blocking Hole-Transport Polyterpenol Thin Films

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**Abstract:** The carrier blocking property of polyterpenol thin films derived from non-synthetic precursor is studied using Electric Field Induced Optical Second Harmonic Generation (EFISHG) technique that can directly probe carrier motion in organic materials. A properly biased double-layer MIM device with a structure of indium zinc oxide (IZO)/polyterpenol/C60/Al shows that by incorporating the polyterpenol thin film, the electron transport can be blocked while the hole transport is allowed. The inherent electron blocking hole transport property is verified using Al/C60/Alq3/polyterpenol/IZO and Al/Alq3/polyterpenol/IZO structures. The rectifying property of polyterpenol is very promising and can be utilized in the fabrication of many organic devices.

**Keywords:** EFISHG, polyterpenol, polymer thin film, organic semiconductors

## Introduction

Recent progress in the area of organic electronic circuits, especially displays, demand new and improved materials for increasing the device efficiency. In electronics, the flexibility, light weight, and efficient integration of the organic materials based electronic devices offer unique attractions [1-2]. Organic electronics present exciting possibilities for the realization of large-area self-illuminating displays based on organic light emitting diodes (OLED) and organic field effect transistors (OFET) [3], organic solar cells [4] and photovoltaic devices, sensors [5], and plastic/organic electronics [6,7]. In OLEDs, holes and electrons are injected from opposite electrodes into an active molecular/macromolecular medium to produce light emission via exciton decay [8]. The efficiency of the OLEDs will be determined by the different layers used in the device; these include hole transport (HTL), emissive (EML), electron transport (ETL) and electron blocking (EBL) layers. Charge transport through the organic layers effect the efficiency of the devices. Therefore it is essential to incorporate additional layers to control both carriers. The HTL plays a significant role in the device performance by maximizing hole injection from the anode while blocking the efficiency-depleting electron overflow from the EML [8, 9].

There are number of hole/ electron transport/ blocking layers are available. HTLs such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOTPSS) [10], polyaniline-camphorsulfonic acid

(PANI-CSA) [11], and polypyrrole-dodecylbenzene sulfonic acid (Ppy-BDSA) [12] have been reported in the literature. The major detriments of many HTLs are only the annealing or ultraviolet photochemical processing requirement but also factors such as low durability and volume shrinkage, or microcracking resulting in leakage current. In the mean time, only very few hole transport electron blocking layers available. Such layers can improve the efficiency of Organic Light Emitting Diodes (OLEDs). A balanced injection and accumulation of charge carriers are essential to improve the efficiency of OLEDs however due to the misalignment of their extremely low-lying highest occupied molecular orbits (HOMOs) against those of organic HTLs, unbalanced charge transport is prevalent. Sun *et al* [9] reported enhancement of efficiency of Quantum Dot LEDs with a high color purity by using multiple holeinjection (HIL)/HTL layers, composed of PEDOT, poly(*N,N*-bis(4-butylphenyl)-*N,N*-bis(phenyl)benzidine (poly-TPD) [or poly(*N*-vinylcarbazole) (PVK) blending with and without poly-TPD], and a salmon-based deoxyribonucleic acid (DNA) complexed with cetyltrimethylammonium (CTMA) to improve the hole transport. The DNA in conjunction with CTMA act as a hole transport electron blocking layer.

Majority of the currently utilized organic precursors used to fabricate charge transport controlling layers pose an environmental hazard, an impediment, which can be overcome using non-synthetic environmentally conscious alternatives. Polyterpenol is a polymer thin film of terpinen-4-ol, a monoterpene component of the essential oils of several plants, with demonstrated good electrical insulating performance. The developed material is characterized by transparency and stability over the environmental variations. Polyterpenol is used as an interfacial layer in the fabrication of a p-type OFET, substantially improving the mobility of the device [13]. The electrical insulating property of polyterpenol in terms of carrier blocking within double-layer MIM devices was further elucidated through time-resolved visualization of carrier motions using the Electric Field Induced Optical Second Harmonic Generation (EFISHG) technique.

## Experiments

The fabrication of IZO/polyterpenol/C<sub>60</sub>/Al double-layer diodes followed the previously outlined methodology [13, 14]. A thin layer of polyterpenol was deposited onto the IZO surface using RF plasma polymerization at a pressure of 100 mTorr, RF frequency of 13.56 MHz, and 100 W RF power. Terpinen-4-ol (Australian Botanical Products) vapors were released into the reactor at a constant rate. The achieved film thickness was 100 nm. Then, a layer of C<sub>60</sub> followed by Al electrode were deposited onto the polyterpenol thin film using vacuum evaporation technique, under a pressure of 10<sup>-5</sup> Torr and a deposition rate of approximately 1 nm/min.

The I-V characteristics of the IZO/polyterpenol/C<sub>60</sub>/Al diode were studied, with Al acting as the reference electrode. As shown in Figure 1a), the characteristics were comparable to those of a rectifying

diode structure, and no hysteresis was observed. The magnitude of the current was similar to the pentacene-polyterpenol structure, which substantiated our previous findings regarding the insulating behavior of polyterpenol thin films. The results suggested that electron injection from Al electrode as well as hole injection from IZO electrode were probable, but electron injection from the IZO electrode and hole injection from the Al electrode were minor. Electron injection and transport through C<sub>60</sub> and hole injection from IZO and transport through polyterpenol was therefore proposed as the mechanism behind the observed phenomenon. However, additional measurements on the structure had to be performed in order to eliminate other potential scenarios, such as electron injection from Al and successive transport through C<sub>60</sub> and polyterpenol, or hole injection from IZO and successive transport through polyterpenol and C<sub>60</sub> layers.

Time-resolved EFISHG can directly probe the carrier motion within the double-layer diodes, providing direct experimental evidence necessary to verify the carrier behavior within such a device. The experimental setup used in this study can be found elsewhere [15]. In the experiment, external voltage ( $V_{ex}$ ) is applied to the double layer with capacitance  $C_i$  and conductance  $G_i$  and charges  $\pm Q_m$  are induced on the electrodes with a response time  $\tau_{RC} = R_s C^*$ , where  $C^*$  is the total series capacitance of the diode. At time  $t \gg \tau_{RC}$ , charge carriers are injected into the device and transported along the direction of the electric field. Should the respective relaxation times between the blocking and the active layers differ,  $\tau_1 \neq \tau_2$ , a charge  $Q_s$  is accumulated at the boundary between these layers with a relaxation time  $\tau_{MW} = (C_1 + C_2) / (G_1 + G_2)$ ,  $\tau_{MW} \gg \tau_{RC}$ , due to the Maxwell-Wagner (MW) effect. The electric field distribution is directly correlated to the SHG signal changes [16, 17].

The EFISHG is distinct in that it is generated in proportion to the square of static electric field, a characteristic that sets it apart from other SHG sources. The expression  $I_{sh} \propto d^2 P(2\omega)^2$  can be used to describe the intensity of the second harmonic signal, with the nonlinear polarization wave  $P(2\omega) = \epsilon_0^{(2)} : E(\omega)E(\omega) + \epsilon_0^{(3)} : E(0)E(\omega)E(\omega)$ , the thickness of the centrosymmetric layer  $d$ , the permittivity of vacuum  $\epsilon_0$ , the average electric field across the probed layer  $E(0)$ , the electric field of the  $p$ -polarized light  $E(\omega)$ , and the  $n^{\text{th}}$ -order nonlinear susceptibility tensor  $\epsilon_0^{(n)}$  ( $n = 2, 3, \dots$ ), which is a material dependent parameter with  $\omega$ . For C<sub>60</sub>,  $\epsilon_0^{(2)} = 0$ , with only the SH generation due to the second term contribution expected to appear. The square-root of SH intensity  $(I_{sh})^{0.5}$  is used for probing the electric field  $E(0)$  which is the square-root of the absolute difference between the SH intensity at the baseline level and under applied external voltage. For C<sub>60</sub>, the wavelength of the probing light is set to 1000 nm, with the SH light intensity  $I(2\omega)$  generated at 500 nm [18]. In this case, we used laser beam without focusing to probe average electric field in the device thickness direction originated from charge charging/discharging at the C60/polyterpenol interface.

Before carrying this EFISHG experiments, it is very important to confirm no SHG generation from terpenol, Al and IZO at a wavelength of 500nm, which is used for probing the SHG generation from the

C60 layer. Using Al/terpenol/IZO diodes, we checked the absorption of the diode with polyterpenol thin film at 500 nm (see the inset of Fig. 1b). Figure 1b shows the intensity of the reflected second harmonic signal for the diode with polyterpenol thin film. As it is exhibited, at the selected wavelengths of the fundamental laser beam (1000 nm) and excited second harmonic electromagnetic signal (500 nm), the polyterpenol based structure has no significant contribution. That is, no SHG generation is expected from polyterpenol thin film layer.

## Results and Discussions

The experimental results of time-resolved EFISHG of the double layer MIM device illustrating the charging and discharging mechanisms are presented in Figure 2(a). During charging, a step voltage was applied to the device, and it was removed in the discharging process. Figure 2(a) illustrates 3 conditions, namely 0 V, 3 V and 5 V on IZO with reference to Al electrode. The changes in the intensity of the SH signal were interpreted in terms of the electric field distribution in C<sub>60</sub> layer under the presence of injected charge carriers [15, 19]. The base line response was obtained for  $V_{ex} = 0$ . For the forward bias conditions of 3 V or 5 V, electron injection into C<sub>60</sub> layer from Al electrode to the polyterpenol layer and/or hole injection into polyterpenol from IZO was suggested [15]. After analyzing experimental data in the manner same as in our previous study, using a filtering method, it was shown that the decaying process during charging satisfied relaxation time dependence of applied voltage  $1/V^2$ . This suggested recombination of electrons and holes at the interface was probable, with the amount of positive charge less than that of negative charge [16]. The SH intensity increased from the baseline and a maximum SH intensity was obtained at  $10^{-6}$  s, on replying electrode charging with a response time  $\tau_{RC}$ . Smooth carrier injection followed, with electrons being transported and accumulated at the C<sub>60</sub>/polyterpenol interface. This was reflected by the rapid decrease in SH intensity to its initial baseline level, which it reached at approximately  $10^{-3}$  s, corresponding to the MW relaxation time  $\tau_{MW}$ . In this case, the electric field was relaxed since charges  $\pm Q_m$  accumulated on electrodes at  $\tau_{RC} = 440$  ns and the charges  $Q_s$  accumulated at C<sub>60</sub>/polyterpenol.

In the case of reverse bias conditions, holes were candidates injected from Al electrode. As can be seen from Figure 2(b), the SH intensity for charging and discharging processes of the device under reverse bias conditions was a distinct feature in comparison with the forward bias. The charges  $\pm Q_m$  accumulated on electrodes at  $\tau_{RC} = 440$  ns, but the  $Q_s$  accumulated at C<sub>60</sub>/polyterpenol was very small. The SH peak was broader in the case of hole injection compared to electron injection, which was in agreement with our previous study [15, 19]. The injection commenced at approximately 1 sec. During the discharge phase of the experiment, first the charges on the electrodes disappeared at 1 sec, while the accumulated electrons stayed at the interface. These results suggested that hole injection was blocked by the C<sub>60</sub> layer, and electron injection was prohibited by the polyterpenol.

The inherent electron blocking hole transport property of the polyterpenol was further corroborated using Al/Alq<sub>3</sub>/polyterpenol/IZO and Al/C<sub>60</sub>/Alq<sub>3</sub>/polyterpenol/IZO structures, schematics for which are presented in Figures 3(a) and 3(b). In the case of Al/Alq<sub>3</sub>/polyterpenol/IZO device, holes from IZO side were transported through the polyterpenol and recombined at the Alq<sub>3</sub> layer with the electrons transmitted from the Al electrode. As a result of this recombination, electromagnetic radiation was emitted, as illustrated in Figure 3(c). Fig 3(c) shows the intensity of the emitted radiation and the photoluminescence measured using a spectrometer (*Andor Technology, SR163*). A study was carried out using the structure shown in Fig 3(b), Al/C<sub>60</sub>/Alq<sub>3</sub>/polyterpenol/IZO. The n-type C<sub>60</sub> promotes the transport of electrons injected from Al electrode and accumulate at the C<sub>60</sub> Alq<sub>3</sub> interface. As in the previous case holes are transported through the polyterpenol layer and a charge recombination happens at the Alq<sub>3</sub> - C<sub>60</sub> layer. The observed intensity and photoluminescence is measured and shown in Fig. 3(c). This study clearly elucidate the charge transport property of the polyterpenol thin film, which is a new environmentally friendly electron blocking layer that can be used in between the active organic layers and anode.

## Conclusions

The charge transport mechanism across plasma polymerized polyterpenol was studied by depositing the n-type organic semiconductor, C<sub>60</sub> on the polyterpenol thin film and Al top electrodes. Using the EFISHG, charge accumulation under the steady state was demonstrated for electron injection from the Al/C<sub>60</sub> ( $V > 0$ ), whereas no charge accumulation was observed for hole injection ( $V < 0$ ) from Al/C<sub>60</sub>. Resulting from these observations, electron blocking property of polyterpenol was proposed as a likely mechanism. Results from electroluminescence spectrum measurement on the Al/C<sub>60</sub>/Alq<sub>3</sub>/polyterpenol/IZO structure evidently confirmed the rectifying property of polyterpenol, with electron and hole recombination taking place in Alq<sub>3</sub> and C<sub>60</sub> layers, indicated by the EL wavelengths of the emitted light consistent with Alq<sub>3</sub> and C<sub>60</sub> photoluminescence spectra. This study substantiate that the environmentally friendly transparent polyterpenol thin film will be an excellent candidate to be used as a ‘hole transport electron blocking layer’ in organic electronic circuits and hence can be utilized in the fabrication of many organic devices, e.g., OLEDs.

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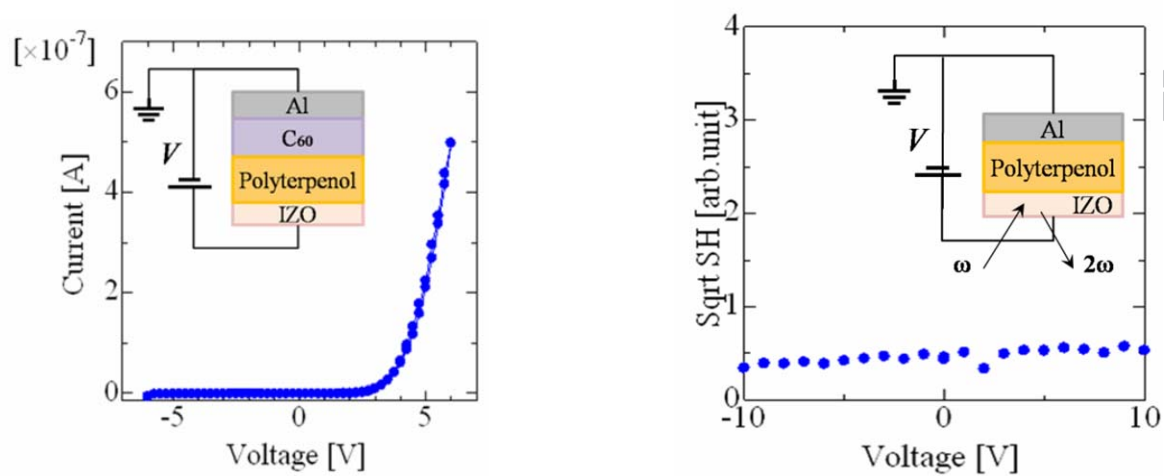


Figure 1 a) The I-V characteristics of the polyterpenol-C<sub>60</sub> double layer device. Inset: The structure of the device. b) The intensity of the reflected second harmonic signal of wavelength 500 nm.



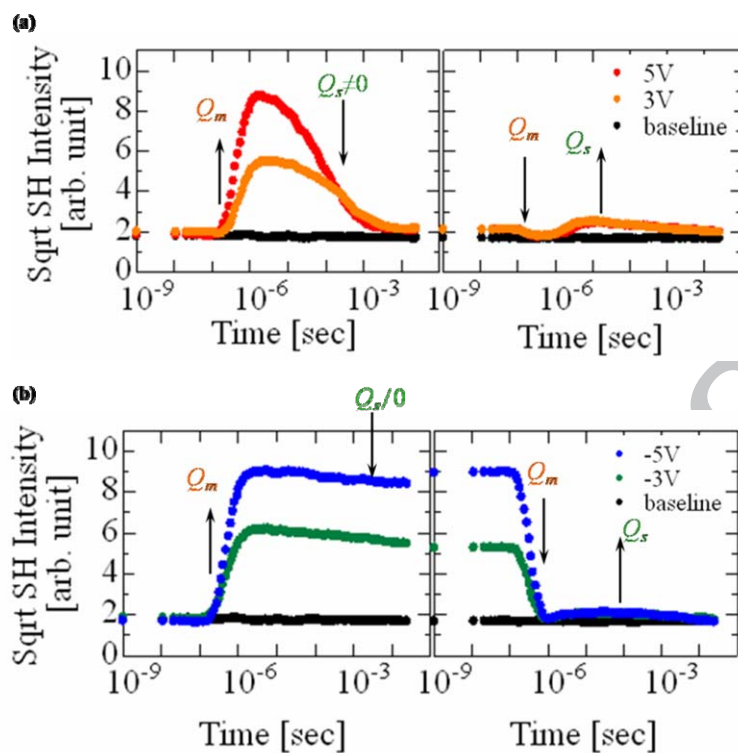


Figure 2. SH intensity for charging and discharging processes of IZO/polyterpenol/C<sub>60</sub>/Al device under forward (a) and reverse (b) bias conditions, and the baseline for SH intensity at  $V_{ex} = 0$ .

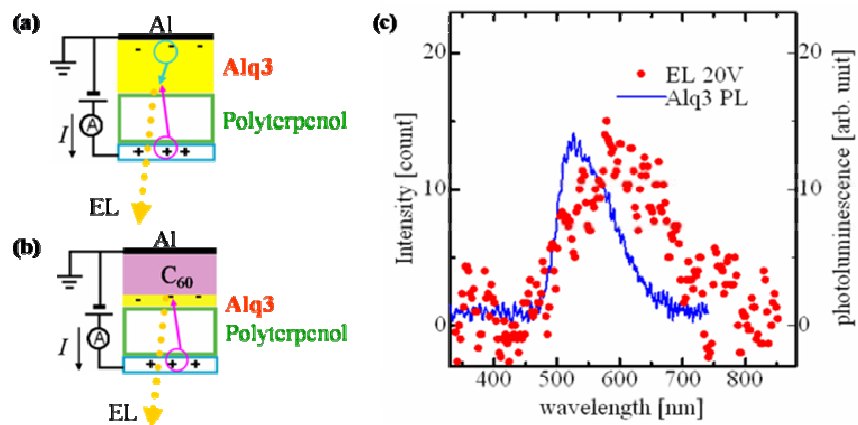
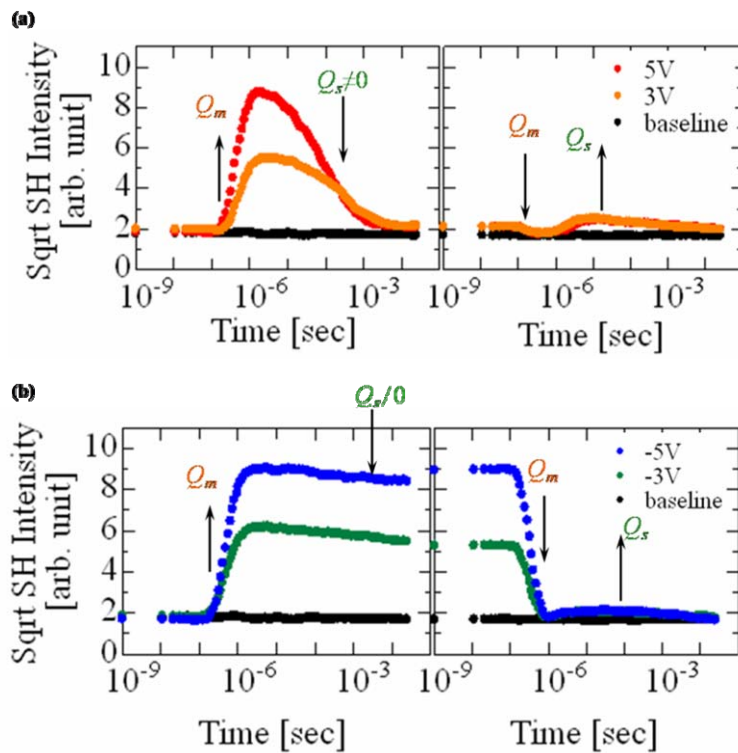


Figure 3. Experimental set-up and device structure (a) Al/C<sub>60</sub>/Alq<sub>3</sub>/polyterpenol/IZO, and (b) Al/Alq<sub>3</sub>/polyterpenol/IZO. (c) Observed electromagnetic radiation as a result of electron-hole recombination at Alq<sub>3</sub> layer.



A polymer thin film is fabricated from non-synthetic terpenol.

EFISHG can directly probe carrier motion in organic materials.

The charge transport through the polyterpenol/C60 structure is investigated

Electron-Blocking Hole-Transport nature of polyterpenol thin film is confirmed.

Novel environmentally friendly polymer thin film for organic electronics.

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