

# Effects of Solvent on Fabrication of Polymeric Light Emitting Devices

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Toluene, chloroform and their mixture have been used as solvents in spin coating for the fabrication of PFO-based polymeric light emitting devices (PLED). Three PL and EL emission components at 420, 440 and 470 nm were observed, with the distribution of PL spectra different from that for EL. The magnitude of the 470 nm component increases in EL spectra while decreases in PL spectra with the introduction of chloroform. On-set voltage of the PLEDs from the toluene solution is the lowest and is the highest from chloroform. The observed results suggested that the difference in solvent polarity, reactivity and vaporizing rate has strong effect on the polymers in solutions, the underlying layer and the cast

## [1] Introduction

Recently, organic thin films have received significant attention for light emission applications. The active organic light emitting layer involving small molecules such as Alq<sub>3</sub> is often deposited by vacuum sublimation whereas low cost spin coating or ink jet printing is employed for devices of large molecules. Using spin coating, it is expected that the preparation conditions (particularly type of the solvent used) will have an impact on the device opto-electronic properties.

It has been reported that both photoluminescence (PL) and absorption spectra of poly[1-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) in chlorobenzene (CB) shifted towards long wavelengths compared with that in tetrahydrofuran (THF) [1]. This shift in PL was attributed to the formation of aggregates, which is solvent dependent. More detailed description of effects of MEH-PPV concentration in CB and THF on PL and EL (electroluminescence) was reported in reference [2]. Recently, results on the studies of a 9,9-diarylated polyfluorenes have also been reported [3]. In that work, PL spectra of a cast film showed three peaks at 2.6, 2.8 and 2.95 eV. A strong and broad peak at 2.3 eV (540 nm) was observed after a photo-oxidation. The magnitudes of the peaks at 2.6, 2.8 and 2.95 eV decreased significantly after further photo-oxidation. These PL results were attributed to keto sites, which occurred on chains and led to enhanced trapping of electrons [4].

In the present work, we have studied two blue emitting polymers CN-PPP: Poly[2-(5-cyano-5-methylhexyloxy)-1,4-phenylene], and PFO: poly(9,9-dioctylfluorenyl-2,7-diyl) in toluene, chloroform and

their mixture. This was done in order to study the effects of solvents and the casting methods.

## [2] Experimental

The conjugated polymers PFO (ADS229BE, Mw=160,000, Mn=70,000) and CN-PPP (ADS220BE, Mw=44,000, Mn=17,000) used are available from American Dye Source Inc. [5]. The fabrication of PLEDs starts from the patterning into 8 stripes of an ITO film on a glass substrate (Applied Films Lab.). After cleaning, a layer of PEDOT (Baytron P, purchased from Aldrich Chemical Corp.) was applied. A layer of CN-PPP or PFO (200 nm) was then spin-coated on the substrate. For comparison, three solutions with toluene (40-1 and 47-1), 40% chloroform + 60% toluene (40-2 and 47-2) and chloroform (40-3 and 47-3) were prepared. Here, 40-1, 40-2 and 40-3 were for CN-PPP whereas 47-1, 47-2 and 47-3 for PFO. After spin coating, the films were dried and loaded into a vacuum chamber for cathode deposition. The cathode consisted of an Mg-Ag layer (100 nm) and an Ag layer (400 nm), which were evaporated sequentially without breaking the vacuum. Current-voltage characteristics of the as-fabricated devices (active area = 0.05 cm<sup>2</sup>) were measured using an HP model 4145A semiconductor analyzer. Among the samples prepared using CN-PPP, 40-1 showed the lowest on-set voltage and was the highest for 40-3. An intermediate on-set value was observed for 40-2. The on-set voltage difference in the PFO devices is even more pronounced, as shown in Fig. 1. Here, 47-1 shows the lowest on-set voltage and 47-3 has the highest value. Both PL and EL spectra were measured on all PLEDs using a Photon Technology International model MD-5020 spectrophotometer.

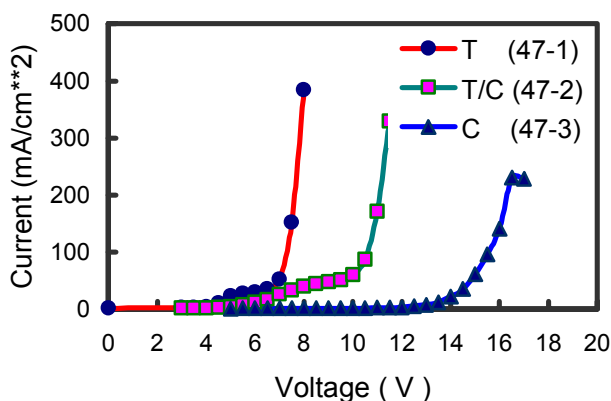


Fig. 1 Current-voltage characteristics of PLEDs fabricated on PFO cast from solutions with toluene (47-1), mixture of 40% chloroform + 60% toluene (47-2) and chloroform (47-3) as the solvent. (T=toluene, C=chloroform)

### [3] Results

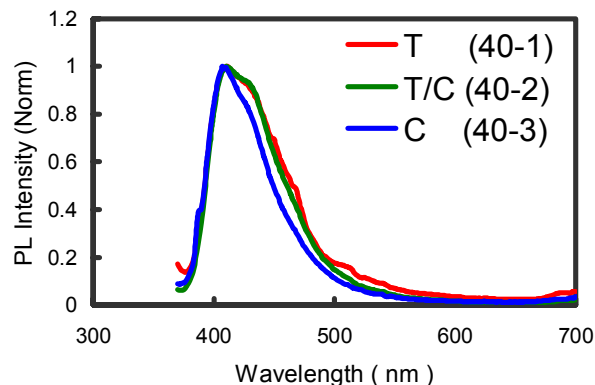
#### [3-1] PL results

For the CN-PPP PLEDs, PL spectra are very similar with peaks at 410 nm. The half height width is about 55 nm for 40-3 with chloroform (Fig. 2a) and with a broadening by 10 – 15 nm for 40-1 and 40-2 (with toluene and toluene/chloroform). For the PFO devices, three PL components can be identified at 420, 440 and 470 nm (Fig. 2b). For 47-1 and 47-2, the dominant peaks are at 440 nm whereas it is at 420 nm for 47-3. The above results suggest that the molecule arrangement in the film cast from the chloroform solution is different from the ones containing toluene. By comparing with PL spectra from a 50 ppm solution in toluene, it is evident that the peaks at 420 and 440 nm are due to the intrinsic characteristics of PFO, which have been previously assigned to the excitonic emission and its vibronic progression from non-interacting single chains [6].

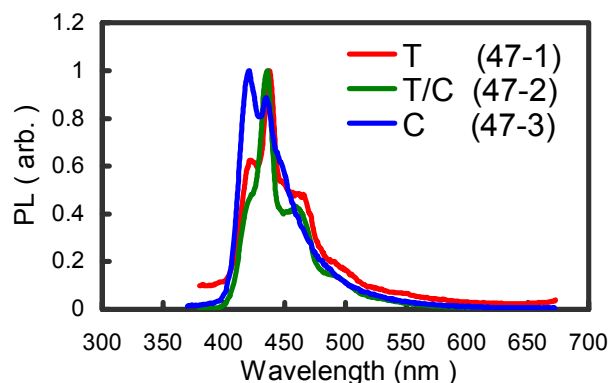
#### [3-2] EL Results

Fig. 3a shows EL spectra from 40-1, 40-2 and 40-3 (CN-PPP PLEDs). For the device 40-1 cast from toluene solution and device 40-2 cast from a mixture of toluene and chloroform, EL is almost the same as that of PL with a peak shift to 415 nm and a half height width of 65-95 nm. However, this is not the case for device 40-3 cast from chloroform solution, for which the EL spectra show a peak at 480 nm with a half height width > 100 nm. Since 40-3 was fabricated under the same conditions as that for 40-1 and 40-2, the results suggest that the cast films are affected by the solvent used. Due to the high vaporization rate of chloroform, the cast film may contain microscopic vacancies. In addition, intermixing may occur between PEDOT and the CN-PPP layer, to result in

the high on-set voltage in PLED fabricated from the chloroform solution (see Fig. 1).



(a)



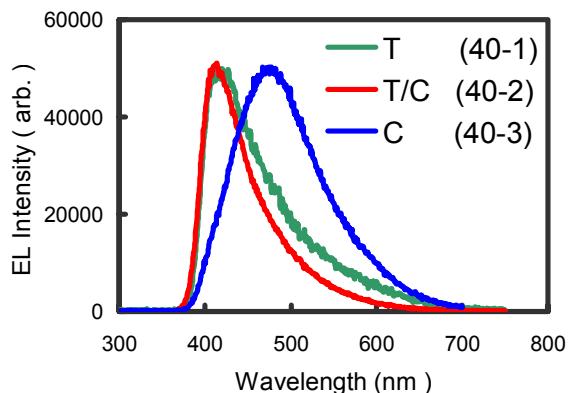
(b)

Fig. 2 PL versus wavelength of the films in the PLEDs fabricated on (a) CN-PPP and (b) PFO.

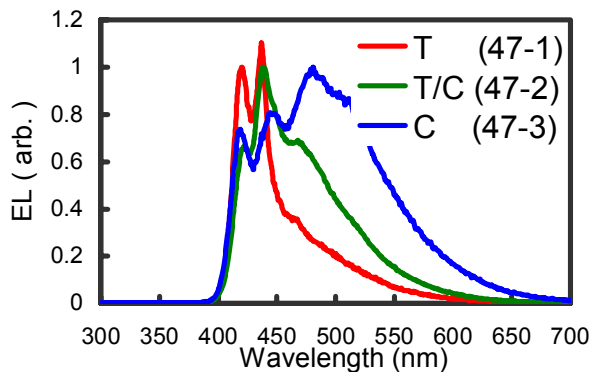
Fig. 3b shows EL spectra of PFO-based PLEDs: 47-1, 47-2 and 47-3. For the device 47-1 made from toluene solution, two main peaks are at 420 and 440 nm plus a visible but very weak component from 450 nm to 650 nm (assigned as 470 nm). For the device 47-2 fabricated from a mixture of toluene and chloroform solution, the 420 nm peak height decreases and the tail intensity increases, with a clear evolution of the 470 nm peak. The magnitude of the 470 nm peak is even greater for the device 47-3 made from chloroform solution. It is also seen that the position of the 470 nm peak shifts to 480 nm, with an evolution of yet another peak at 520 nm (green peak). Hence, in addition to the intrinsic peaks at 420 and 440 nm, long wavelength components at 480 nm appear in the film cast from chloroform due possibly to aggregate formation. This is opposite to the trend seen in PL spectra.

It is thus clearly seen that the effect of solvent on PL obviously is different from that on EL. The EL results

observed from the present CN-PPP and PFO polymers are not consistent to that described in [2], where it was reported that the degree of aggregates in the films was proportional to the solutions used for the film casting. It is also important to note that the impact of solvent on the pre-deposited PEDOT layer and on the morphology of the cast emissive layer cannot be ignored. Research work is being continued to establish relationship between such a solvent effect and the I-V characteristics of the fabricated PLEDs as shown in Fig. 1.



(a)



(b)

Fig. 3 EL versus wavelength for the PLEDs shown in Figs. 1 and 2 cast from (a) CN-PPP solutions and (b) PFO solutions.

#### [4] Conclusions

It has been observed that the PL and EL characteristics for PLEDs fabricated under the same conditions from CN-PPP and PFO with different solvents are different. The PL spectra of CN-PPP based PLEDs show a single peak at 410 nm, with the narrowest half height width for chloroform. However, the EL results on the same PLEDs show significant broadening in the spectra with a peak shift from 415 to 470 nm along with

the change of solvent from toluene to chloroform. Although the EL spectra of PLEDs on PFO revealed more complicated features than those on CN-PPP, a similar solvent effect was observed. From the toluene solvent to chloroform solvent, the EL generally shifts to longer wavelengths.

Current-voltage characteristics on the CN-PPP and PFO PLEDs fabricated also show a consistent trend of increase of the on-set voltage: toluene < toluene chloroform < chloroform.

The above two trends with respect to the solvent effect observed independently from two different light emitting polymers imply that the effect of solvent on processing could not be ignored. This effect is believed to be a result of different degree of interactions between the polymer and the PEDOT layers. The more severe inter-mixing between PEDOT and the polymer from chloroform may have led to an increase in potential barrier for holes. Alternately, the usage of chloroform may have created a polymer film with microscopic vacancies and excessively large resistivity causing a shift in Fermi level of the polymers.

As a further conclusion, the results presented in this communication support the argument that the emission peaks of 420 nm and 440 nm are due to intrinsic properties of PFO, whereas the emission peak of 470-480 nm is related to aggregation or  $\beta$ -phase formation [3]. However, the origin and nature of the emission peak at 520 - 540 nm are still not certain and are subjects of further investigation [7].

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