Preparation of Insoluble Hole-Injection Layers by Cationic Ring-Opening Polymerisation of Oxetane-Derivatized TriPhenylamineDimer for Organic Electronics Devices

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Abstract

We have demostrated that oxetane-derivatized hole conductors as well as electroluminescent polymers can be crosslinked via cationic ring-opening polymerisation (CROP) without deterioration of their electrical and electro-optical properties. This allows the fabrication of electronic multilayer devices via solution process. Here, we demonstrate three kinds of CROP crosslinking methods. They are (1) oxidative crosslinking, (2) photo crosslinking, and (3) trityl crosslinking. The crosslinking process parameters as well as the fluorescence characteristics and the solvent resistance of the resulting films have been investigated. The result shows that the oxidative crosslinking (1) gives the possibility to obtain the doping effect which increases the conductivity of the insoluble layer, although it reduces the fluorescence characteristics. The photo crosslinking (2) is controlled by irradiation; therefore, it gives the possibility to pixelate or pattern the film (lithography). It shows less fluorescence quenching than in (1). The trityl crosslinking (3) is suitable for the devices which are not pixelated and do not need the doping effect. Irradiation is not applicable here. Finally, we applied the insoluble layers in hole-only devices and blue-emitting OLEDs. We found that introduction of the layers improves the efficiency of the OLEDs.

1. Introduction

Organic electronic devices had a rapid progress in the recent years. Organic light-emitting diodes (OLEDs) are important in display and lighting applications. The OLEDs can be fabricated via vacuum evaporation or solution processing, e.g. spin coating (printing in general). The solution process offers

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some advantages like the possibility for large-area and low-cost fabrication. However, it has a crucial problem in multilayer device fabrication where the first layer will be dissolved by the solvent of the second layer.

In this paper we introduce the preparation of insoluble layers through crosslinking of oxetane-derivatized materials for device preparation via solution processing. The principle of crosslinking is based on cationic ring-opening polymerisation, Figure 1. This polymerisation is initiated by oxetane ring opening. In this case, the oxetane ring acts as nucleophile and is opened in the reaction with an electrophile.

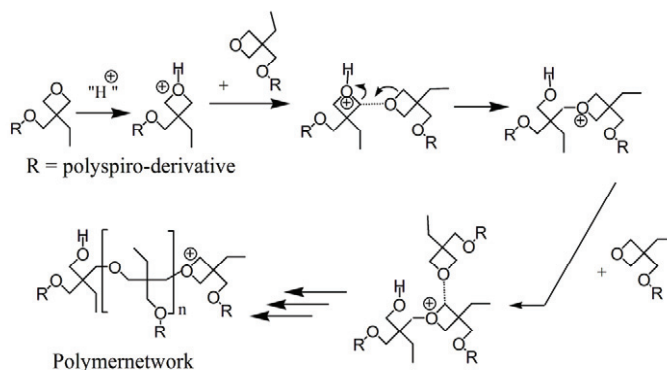R = polyspiro-derivative

Polymernetwork

Fig. 1. Cationic ring-opening polymerisation of oxetanes

Three kinds of crosslinking mechanism with different initiator are introduced in this paper. They are oxidative crosslinking (1), photo crosslinking (2), and trityl crosslinking (3). The insolubility resulting from the crosslinking is tested as solvent resistance. We report also the fluorescence characteristics of crossliked films as quenching effect, and the application of cross linked-films in hole-only devices and blue-emitting OLEDs.

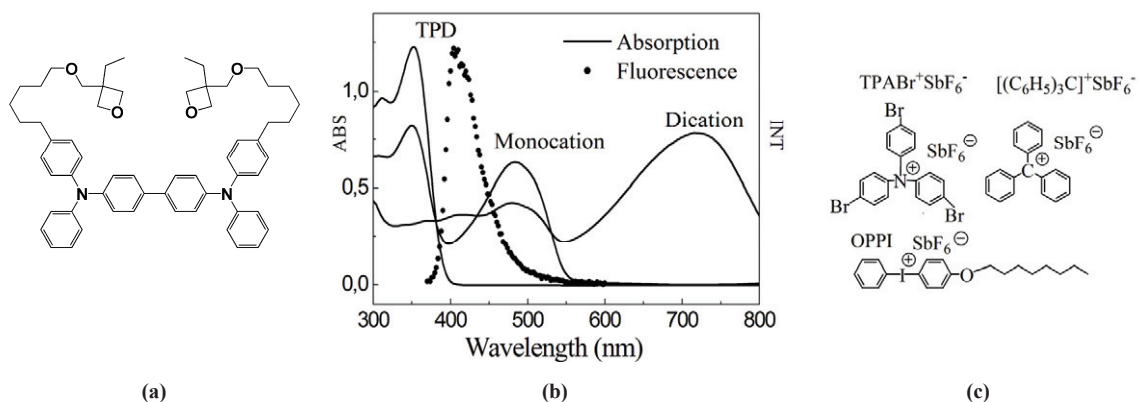(a)   (b)   (c)

Fig. 2. (a) Molecular structure of XTPD, (b) The electro-optic characteristics of TPD, (c) The initiators

The crosslinkable material used in this work is a hole (defect electron) conductor based on oxetane-derivatized TriPhenylamineDimer (XTPD). The oxidants in oxidative crosslinking (1) are nitrosonium-hexafluoroantimonate $(NOSbF_6)$, tris(4-bromophenyl)aminium-hexafluoroantimonate $(TPABrSbF_6,)$

and silver-hexafluoroantimonate (AgSbF$_6$). As photoinitiator in photocrosslinking (2) we used 4-octyloxydiphenyliodonium hexafluoroantimonate (OPPI), and the salt in trityl crosslinking (3) is tritylium-hexafluoroantimonate [C(C$_6$H$_5$)$_3$SbF$_6$]. These oxidants, photoinitiator, and salt will be referred to as initiator. The organic layers in this work were prepared via spincoating. The molecular structures of materials and electro-optic characteristics of TPD are shown in Figure 2.
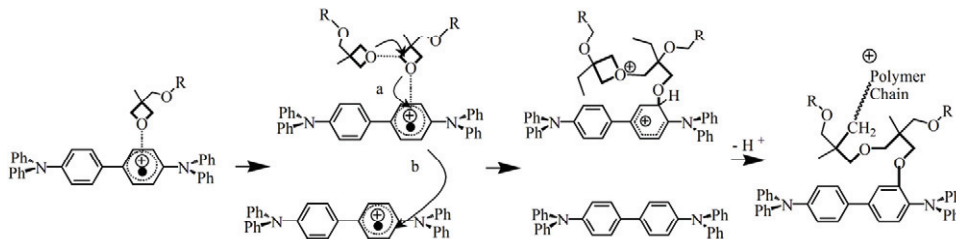

Fig. 3. Oxidative crosslinking mechanism

The crosslinking process in the oxidative crosslinking (1) is initiated by the oxidation of XTPD which produces the cationic radical species (TPD$^{+\bullet}$). This TPD$^{+\bullet}$ acts as an electrophile and at least two TPD$^{+\bullet}$ are needed to start the crosslinking reaction (Figure 3). They have two possibilities to react with the oxetane. Firstly, the oxetane attacks the first TPD$^{+\bullet}$ and then an electron is transferred to the second TPD$^{+\bullet}$ to find a stable product (Figure 3). In the second possibility, an electron from the first TPD$^{+\bullet}$ is transferred to the second TPD$^{+\bullet}$ resulting in TPD^{++} and TPD (disproportionation). Then, the oxetane may attack the TPD^{++} (Figure 3). These reactions are followed by opening the oxetane ring. Finally, a proton is abstracted, and it can initiate another chain by acting as an electrophile. Overall, two TPD$^{+\bullet}$ start two polymer chains.
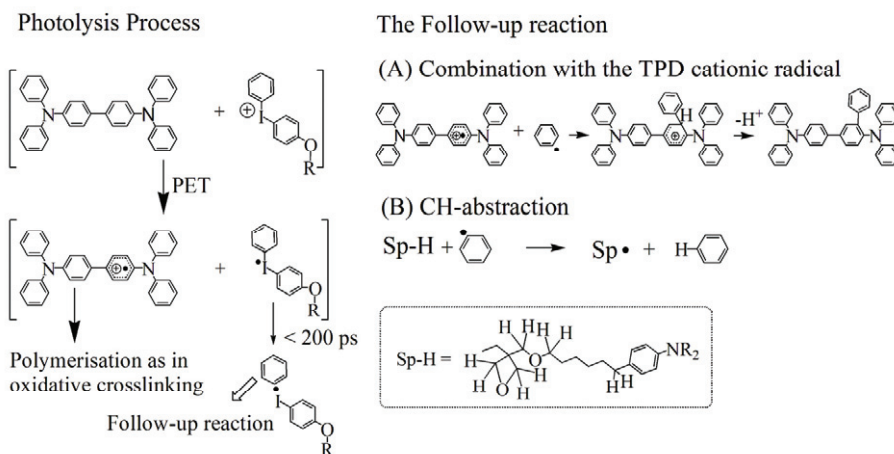

Fig. 4. Photo crosslinking mechanism

The photo crosslinking (2) is initiated by photolysis between XTPD and the iodonium (generally onium) photoinitiator via irradiation with 365 nm UV-light. The reaction produces TPD$^{+\bullet}$ and iodonium

radicals. The iodonium radicals have very short life time (< 200 ps)[4] and decompose very fast and irreversibly by breaking of the C-I bond in phenyliodonium and phenyl radical, Figure 4. This phenyl radical may react with $TPD^{+\bullet}$ in a follow-up reaction A and generates a proton, Figure 4. This proton can open an oxetane ring to initiate the polymerisation. The phenyl radical might react with alkyl spacer by H-abstraction in follow-up reaction B, Figure 4. The follow-up reaction B is non-desired reaction in the photo crosslinking, leading to uncontrolled radical reactions. The other reaction possibility is the reaction between oxetane and $TPD^{+\bullet}$ as in oxidative crosslinking. The trityl crosslinking (3) takes place in analogy to the photon-induced polymerisation.

2. Experiment

The UV-Vis measurement of neutral and oxidized XTPD show the absorption band of the neutral molecule at around 354 nm, the absorption bands of monocation at 477 nm, and the absorption band of dication at 722 nm, Figure 2. This result is in agreement with the result of spectro-electrochemical investigation. Finally, fluorescence measurement shows the luminescence peak of neutral molecule at around 400 nm.

The irradiation and thermal curing investigations were carried out by preparing several series of samples. These samples were prepared from XTPD solutions containing 1.7% mole $AgSbF_6$, 0.8% mole OPPI, or 1.7% mole trityl salt as initiator in the oxidative crosslinking, photo crosslinking, and trityl crosslinking respectively. The irradiation and curing investigation in oxidative crosslinking were carried out without irradiation (1), with 365 nm UV-light irradiation (2) and with 470 nm blue-light irradiation (3). These wavelengths correlate with the absorption of TPD neutral molecule and TPD cationic radical. In the photo crosslinking and trityl crosslinking, only UV-light (365 nm) irradiation is appropriate. The irradiation was carried out for 10 sec for each series. Each series in this investigation consists of two samples, one sample without heat treatment (A) and one sample with 100 °C for 1 min heat treatment (B).

How much of the initiator is needed to find 100% solvent resistance was investigated in the experiment with various amounts of initiator. Various amounts of initiator from 0.03% mole until 3.3% mole were added to the XTPD solution. Films of around 100 nm thickness were prepared via spincoating on glass substrates. The crosslinking process was done through irradiation at 365 nm for 10 sec, followed by curing at 100 °C for one min before the solvent resistance of films was proved. The solvent resistance of films was investigated by comparing the UV-Vis absorption spectra of the crosslinked films, before and after rinsing the films with organic solvent (e.g. tetrahydrofuran - THF).

In the investigation of fluorescence characteristics, XTPD films of about 100 nm thickness on glass substrates with 0%, 1.7%, 2.5% mole of oxidants ($NOSbF_6$, $AgSbF_6$, $TPABrSbF_6$), photo-initiator (OPPI) and $C(C_6H_5)_3SbF_6$ were prepared. The crosslinking was carried out through irradiation with 365 nm UV-light for 10 sec and then curing at 100 °C for one min. The emission spectra were recorded for all of the films and the quenching effect was presented as Stern-Vollmer diagram. The emission intensity of a film with 0% mole photo-initiator was used as reference (I_o).

The insoluble hole-transport layers for hole-only devices (HOD) were prepared via oxidative crosslinking, photo crosslinking and cationic crosslinking with 1.7% mole $TPABrSbF_6$ (HOD1), OPPI (HOD2) , and $C(C_6H_5)_3SbF_6$ (HOD3) as oxidants, photoinitiator, and electrophile agent via standard procedure. Finally, the crosslinked films were rinsed with THF before ca. 100 nm Ag were deposited as cathode.

The multilayer OLEDs were prepared by inserting the insoluble hole-transport layer (HTL). As emitter a blue-emitting polymer based on polyfluorene is used. The insoluble HTLs were prepared through photo-crosslinking with 3.3% mole OPPI to build up the multilayer devices, OLED1 with

ITO/PEDOT/HTL1/blue-emitter/Ba/Ag structure. The characteristics of device are compared with single layer device, ITO/PEDOT/blue-emitter/Ba/Ag (OLED0) as reference.

3. Results and Discussion

The results in Table 1 show that in oxidative crosslinking without heat treatment (samples A), the irradiation with 365 nm UV light gives better results than the irradiation with 470 nm blue light and without irradiation.

Table 1. The solvent resistance as result of irradiation and curing treatment

Temperature	Solvent Resistance (%)						
	Oxidative crosslinking (1)			Photo crosslinking (2)		Trityl crosslinking (3)	
	No Irr	470 nm	365 nm	No Irr	365 nm	No Irr	365 nm
25 °C	10	41	61	1	77	96	96
100 °C	98	98	98	3	99	100	100

According to the TPD absorption spectra in Figure 2, the irradiation with 470 nm might excite an electron from the SOMO level to the LUMO level in the TPD radical cation (TPD$^{+\bullet}$). Then, two excited cationic radical lead to the formation of a TPD dication (TPD^{++}) and a TPD neutral molecule via disproportionation. Against nucleophile, TPD^{++} is generally more reactive than cationic radical. As a consequence, it makes the initiation process (ring opening of oxetane) easier, or faster than without irradiation, but less than irradiation with 365 nm.

The UV-light (365 nm) irradiation may excite more electronic transitions in the TPD neutral molecule. Firstly, an electron in TPD neutral molecule will be excited from HOMO level to the LUMO level. This electron can relax to the HOMO level and release the energy to the neighboring TPD radical cation (TPD$^{+\bullet}$). In this case, the transfer of energy is possible, because of the high density of molecules in the amorphous films and the overlapping between neutral molecule fluorescence and cationic radical absorption band. Furthermore, an electron is excited from SOMO-level to the LUMO-level in this TPD$^{+\bullet}$ by energy transfer during electron re-absorption reaction in excited neighbored neutral molecule. This reaction will be followed by the same reaction of blue light irradiation and results TPD^{++} and TPD. Secondly, the 365 nm irradiation has also the possibility to excite directly an electron in TPD cationic radical, Figure 2. As known, the temperature can increase the reaction rate. Therefore, curing treatment gives significantly better result than without curing treatment.

In the photo crosslinking process without irradiation, the solvent resistance is essentially zero, even for curing at 100 °C. The best solvent resistance is obtained by irradiation with 365 nm UV-light. Through irradiation, the crosslinking is started by photolysis process which results TPD$^{+\bullet}$ and phenyl radical. Then, the H$^+$ is produced in the reaction between TPD$^{+\bullet}$ and phenyl radical. Furthermore, the oxetane opening ring will be induced by H$^+$ or by TPD$^{+\bullet}$ as like in the oxidative crosslinking. This result is in agreement with the crosslinking mechanism in Figure 4.

The fact that the photo crosslinking is strongly controlled by irradiation offers the possibility to do pixelation or patterning. The illuminated area on the OLED for example can be crosslinked through this mechanism and the non-illuminated area can be dissolved easy by organic solvent. Furthermore, the curing treatment at 100 °C for one min gives the better result than without curing treatment.

The experimental results in the trityl crosslinking show that there is no effect of irradiation on the solvent resistance, and curing treatment at 100 °C for one min gives only slightly better result. This result

is in agreement with the mechanism in Figure 3c, where the trityl cation as electrophile reacts directly with an oxetane. Therefore, as expected, there is no influence of irradiation.

The solvent resistance of oxidative crosslinking, photo crosslinking, or trityl corsslinking increases exponentially with the amount of oxidant, photoinitiator, or trityl salt. By using more than 1% mole oxidant, photoinitiator, or trityl salts these three crosslinking processes produce around 100% solvent resistance by irradiation with 365 nm for 10 sec and curing at 100 °C for one min.

For comparison, we assumed the fitting equation as:

$$y = y_0 (1 - \exp(-[x]/x_o))$$

where y_0 is the maximum result (100%), x is the amount of oxidant in % mole, and x_o is the amount of oxidant in % mole to obtain 63% solvent resistance according to the value $1/e = 0.37$.
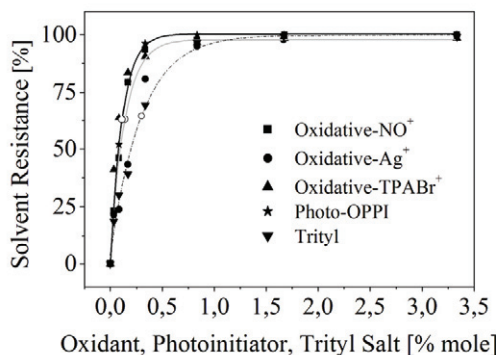

Fig. 5. The solvent resistance characteristics regarding to the amount of initiators

According to their x_o value, photo crosslinking (x_o=0.11) has the highest efficiency followed by oxidative crosslinking (x_o=0.14), and trityl crosslinking (x_o=0.30). This result is in agreement with the crosslinking mechanism in Figure 3. The photo crosslinking is faster than the oxidative crosslinking in generate H^+ abstraction. In both, photo crosslinking and oxidative crosslinking, the first oxetane ring can be opened by proton and/or by $TPD^{+\bullet}$. In trityl crosslinking this first oxetane ring is opened only by trityl cation. The results above apply for crosslinking at 100 °C curing treatment for one min.

The crosslinking process at room temperature (without curing treatment) can result more than 90% solvent resistance through photocrosslinking and trityl crosslinking with a larger initiator amount. For example, 3.33% mole photo initiator (OPPI) or trityl salt ($C(C_6H_5)_3SbF_6$) is needed to obtain about 95% solvent resistance even without curing. This amount is about 10 times higher than the initiator needed in photo crosslinking with curing treatment, and about 4 times higher than in trityl crosslinking with curing treatment. In other case, oxidative crosslinking cannot obtain 100% solvent resistance without curing treatment. Although its solvent resistance is also exponential dependently on the oxidant amount, its maximum value is only about 80%.

The experimental results above show that the oxidative crosslinking is strongly temperature controlled, photo crosslinking is strongly irradiation controlled, and trityl crosslinking is slightly temperature controlled but not irradiation controlled.

The PL investigation shows that oxidative crosslinked films have the highest quenching effect followed by the photo crosslinked films, and trityl crosslinked film. The oxidative crosslinked films with $NOSbF_6$ as oxidant shows a higher quenching effect than with $AgSbF_6$ or $TPABrSbF_6$ oxidant at the same molar concentrations. In other investigation, the UV-Vis spectra of oxidized solution show similar absorption

bands of the cationic radical in XTPD solution with same amount of $NOSbF_6$, $AgSbF_6$, or $TPABrSbF_6$. According to this result, their quenching effect caused by $TPD^{+\bullet}$ might be similar. The quenching effect caused by counter ion is also similar because they used the same kind and amount of counter ion. Predictably, a higher quenching effect on $NOSbF_6$-films is caused by the higher quenching of NO^+ compared to that of Ag^+ or $TPABr^+$ and also by the presence of its side product and also by presence of its side product [5].

Table 2. Quenching effect of various crosslinked films

Initiator (% mole)	Quenching Effect (Io/I)				
	Oxidative crosslinking (1)			Photo crosslinking (2)	Trityl crosslinking (3)
	$NOSbF_6$	$AgSbF_6$	$TPABrSbF_6$	OPPI	$C(C_6H_5)_3SbF_6$
0	2	1	1	1	1
1.7	5.81	2.73	2.08	1.32	1.04
2.5	8.86	4.8	6.7	1.42	1.2

Photo crosslinked films have lower quenching effect compared to oxidative crosslinked films. According to the crosslinking mechanism in Figure 4, the amount of $TPD^{+\bullet}$ is lower in photo crosslinked films compared to the oxidative crosslinked films.
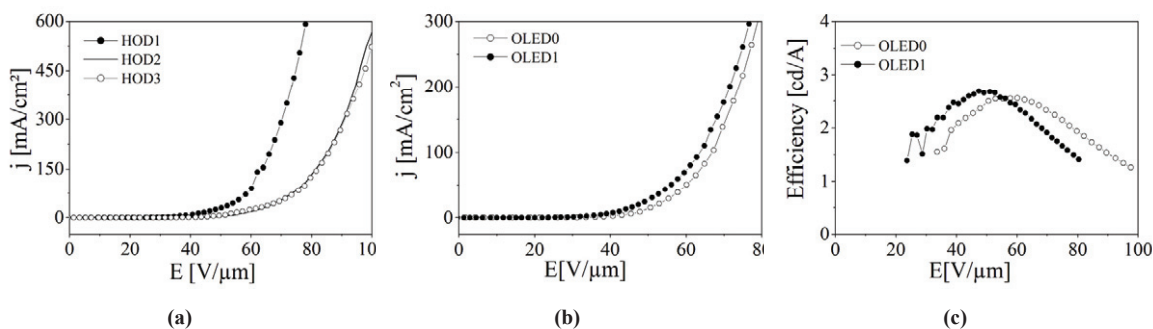

Fig. 6. (a).The doping effect of oxidative crosslinking on HOD1, (b) The current voltage characteristics of OLED0, and OLED1, (c) the efficiency of OLED0 and OLED1

As expected, the trityl crosslinked films have the lowest quenching effect. Independent investigation in solution indicates no oxidation reaction of XTPD by adding the trityl salt. Therefore, $TPD^{+\bullet}$ is not included in this reaction. The oxetane ring is opened directly by the trityl cation. The very low quenching effect on the trityl crosslinked film is related to the presence of counter ion SbF_6^- (and any impurity in the trityl salt). The trityl salt in this experiment is not commercially available and was prepared by adding $AgSbF_6$ to the $C(C_6H_5)_3Cl$ solution [5].However, we cannot entirely exclude, some Ag^+ is still present. The reduction of the photoluminescence intensity in crosslinked films is caused predominantly by the presence of $TPD^{+\bullet}$, but other impurities like the counter ion (SbF_6^-) cation or other species produced in crosslinking reaction can also cause quenching of luminescence.

In Figure 6a, the current density of HOD1 was higher than the current density of HOD2 and HOD3 at a given operating voltage. It was caused by the difference of conductivity of crosslinked films due to the presence of $TPD^{+\bullet}$ as charge carrier in the HTL. This fact indicated that the crosslinking mechanism changes the crosslinked-HTL conductivity which depends on the charge density ($TPD^{+\bullet}$) in HTL.

The current-voltage characteristic in the Figures 6b-c show that the OLED1 had better performance than single layer OLED0. According to the oxidative crosslinking mechanism and solution measurement result, the amount of $TPD^{+\bullet}$ is proportional to the amount of oxidant. Although the current density of the device increases with the amount of charge carrier ($TPD^{+\bullet}$), it is not followed by the increasing of device efficiency. When the recombination happens in interface between HTL and emitter, the photo-luminescence efficient (η_{PL}) should be reduced by quenching effect. Therefore, the efficiency of OLED is reduced. In this case, the OLED efficiency can be improved by inserting a thin blocking layer (un-doped layer) between doped hole-transport layer (DHTL) and emitter [7,8].

4. Conclusion

Insoluble hole-transport layers based on TriPhenylamineDimer (TPD) have been prepared via three crosslinking mechanisms. They are oxidative crosslinking (1), photo crosslinking (2), and trityl crosslinking (3). The oxidative crosslinking (1) gives the possibility to obtain the doping effect which increases the conductivity of the insoluble layer, although it also results in a higher quenching effect in film than the other crosslinking mechanisms. The photo crosslinking (2) is strongly controlled by irradiation, therefore it gives the possibility to pixelate or pattern a film (lithography). It shows a lower quenching effect than that in an oxidative crosslinked film. Finally, the trityl crosslinking (3) is suitable for the devices which are not pixelated and do not need the doping effect. It does not show the quenching effect in the crosslinked film. Irradiation is not applicable in this crosslinking process. Thermal curing treatment can give a better result but it is not essential.

These insoluble layers give the possibility to fabricate multilayer electronic-devices via solution processing. The electrical characteristics of hole-only devices based on crosslinked TPD layer shows the relation of $TPD^{+\bullet}$ with the current density of device. In addition, the application of crosslinked TPD-layer in blue-emitting OLED improved the OLED efficiency.

Acknowledgement

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