

Communications

Molecularly Doped Polymeric Network Nanolayers for Organic Light-Emitting Devices

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Introduction

For a couple of decades a keen interest has been paid to organic light-emitting devices (OLED) that utilize organic semiconductors (small molecules or polymers) as an electro-optical medium.¹⁻³ Recently the device efficiency issue, which was one of the crucial points for low power consumption displays in portable electronic applications, has been almost sorted out by making use of triplet emissions.⁴ However, the commercialization of OLED is still awkward and very limited to a small size display because the device reliability (lifetime) lags behind the criteria of consumer electronics, even though it has been improved by device engineering such as accelerated pre-oxidation method (APOM).⁵ This teaches us a concrete lesson that enhancing device reliability depends critically on the intrinsic property of organic semiconductor materials which includes chemical, physical, and thermal stabilities. In this regard, we have extensively studied thermally stable polymers and hybrid composite systems using epoxy groups were tried as a hole injection/transport layer for OLEDs for the first time,⁸ even though similar but different trials were reported recently regardless of resulting performances.⁹

In this communication we have fabricated OLEDs with molecularly doped polymeric network (MDPN) nanolayers which were made by the thermo-chemical crosslinking

reaction between epoxidized cresol novolak and phenolic novolak in the presence of hole-transporting small molecules. Here the current density - voltage - luminance (J-V-L) characteristics of OLEDs are briefly reported to understand the role of thermo-chemical crosslinking reaction in the MDPN nanolayers. The result showed that the turn-on voltage of OLED was remarkably reduced to ~5 V by the crosslinking reaction, exhibiting >1,000 cd/m² at 11 V despite low loading of hole-transporting molecules.

Results and Discussion

In order to make the MDPN nanolayers, first a novolak epoxy resin was prepared by mixing of epoxidized cresol novolak and phenolic novolak at the same molar ratio. Then the novolak epoxy resin and *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl) benzidine (TPD) were dissolved in tetrahydrofuran by adding a catalytic amount of triphenyl phosphine as an accelerating agent for crosslinking reaction (see Figure 1 for corresponding chemical structures). This mixture solution was vigorously stirred to a clear solution at room temperature. The weight ratio of TPD to novolak epoxy resin was 25:75, whilst the solid concentration of solution was 1 wt%.

The solution was spin-coated onto the ITO-coated glass substrates at 3,000 rpm for 3 min (note that the ITO-glass substrates were pre-cleaned in the same way as in ref. 5), followed by soft-baking at 50 °C for 4 hr. This process resulted in the precursor films (thickness, *t* = 35 nm). One set of the precursor films was kept for device fabrication, whilst

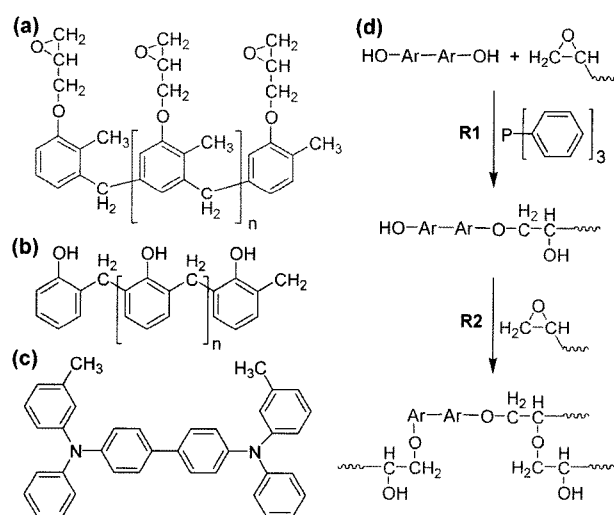


Figure 1. Chemical structures of materials used for molecularly doped polymeric network nanolayers: (a) epoxidized cresol novolak, (b) phenolic novolak, and (c) TPD. (d) Schemes for the thermo-chemical crosslinking (curing) reaction: R1 and R2 denote each step reaction.

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another set was thermally crosslinked (cured) at 160 °C for 20 min to have the MDPN nanolayer ($t=25$ nm). On top of these films, tris(8-hydroxyquinolino) aluminum (Alq₃) ($t=40$ nm) was deposited by thermal evaporation in a vacuum of 5×10^{-6} Torr. Finally, the Al cathode ($t=200$ nm) was deposited on the Alq₃ layer at the same vacuum condition, defining the active emission area of 1.6 cm². Hereafter, the OLEDs with the uncured (MDPN precursor) nanolayer and the cured MDPN nanolayer are called ‘uncured device’ and ‘cured device’, respectively. The J-V-L characteristics of devices were measured using a custom measurement system equipped with an electrometer (Keithley 6517) and luminance meter (Topcon BM-8). The electroluminescence spectra were collected using a fiber-optic spectrometer (Ocean Optics S2000) equipped with a calibrated linear array charge coupled device (CCD) detector.

As shown in Figure 1(d), the chemical crosslink is initialized by the ring opening reaction of epoxy groups in the epoxidized cresol novolak with the hydroxyl groups in the phenolic novolak (see R1 in Figure 1(d)). After this initialization the second crosslinking reaction (R2) occurs at the high temperature condition. This simultaneous curing reaction eventually results in the chemically crosslinked network structure that effectively binds the TPD molecules in between the chains of epoxidized cresol novolak and phenolic novolak units, leading to the improved stability of nanolayer (particularly, of TPD molecules). After this curing reaction, almost no shrinkage (i.e. no thickness change) was observed for the MDPN nanolayer by thermal shock experiments at temperatures lower than the curing condition.

As shown in Figure 2(a), the threshold voltage for charge injection/transport was 5 V for the cured device and 15 V for the uncured device. In addition, the up-turn shape of J-V curves is much steeper for the cured device than for the uncured device. This huge change for the threshold voltage and the J-V curve shape is basically explained by the reduced thickness from 35 to 25 nm by the thermo-chemical crosslinking reaction because the thinner the polymeric nanolayer the lower the bulk resistance. About 67% reduction of the threshold voltage is expected, for the thickness decrease of the nanolayer by about 29% in comparison to that of the precursor film before curing, if the threshold voltage is assumed to be linearly correlated with the thickness of nanolayers. Therefore, additional 38% reduction in the threshold voltage can be assigned to the change of charge (hole) transport characteristics upon the crosslinking reaction, which could be possible by the nanomorphology change as shown in Figure 3(b,c) assuming the unchanged charge injection barrier between ITO and nanolayers (specifically TPD) (see Figure 3(a)).

In more detail, before the curing reaction the TPD molecules are dispersed in the mixture of epoxidized cresol novolak and phenolic novolak in a molecular or slightly

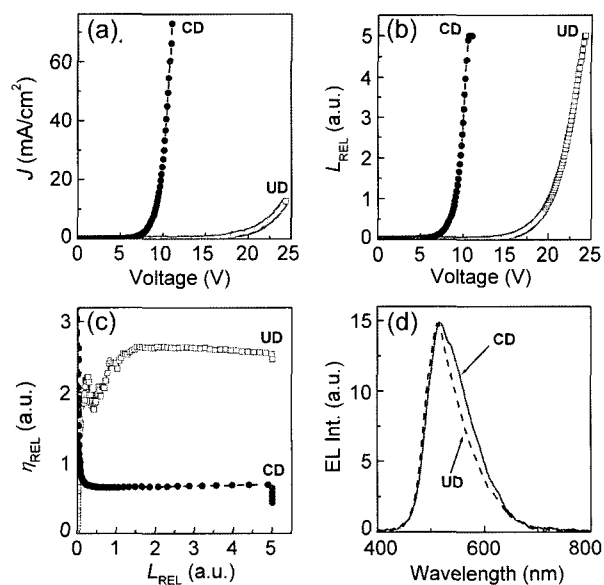


Figure 2. (a) Current density (J)-voltage, (b) relative luminance (L_{REL})-voltage, (c) relative current efficiency (η_{REL})-voltage, and (d) electroluminescence spectra of devices: ‘UD’ and ‘CD’ denote the OLEDs with uncured and cured MDPN nanolayers, respectively. Using a luminance meter $\sim 1,000$ cd/m² was measured at 11 V for the cured and at 25 V for the uncured device.

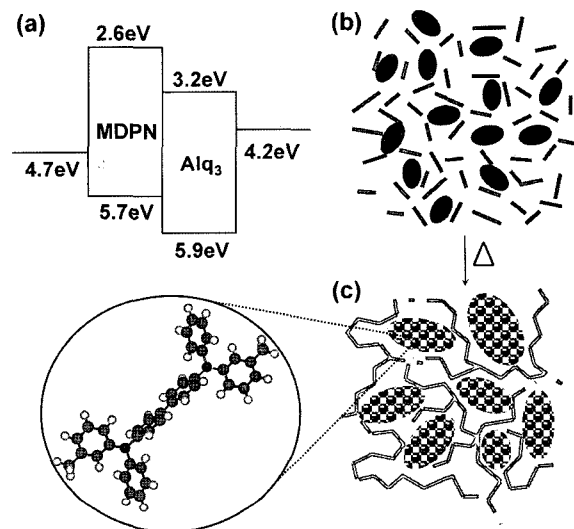


Figure 3. (a) Ideal flat energy band diagram of OLEDs fabricated using uncured (b), and cured (c) MDPN nanolayers. Here we note that (b) and (c) are schematic illustrations to show the nanomorphology change upon the curing reaction: Green rods (b), blue filled ellipsoids (b), red strings (c), and blue-white dotted ellipsoids represent the monomers (epoxidized cresol novolak and phenolic novolak), the TPD molecules dispersed molecularly, the chemically crosslinked chains between the monomers (epoxidized cresol novolak and phenolic novolak), and the TPD aggregates (see the enlarged energy minimized molecular structure of TPD in circle), respectively.

larger scale (see Figure 3(b)). These molecularly separated TPD molecules make billions of gaps between TPD molecules which act as an integrated charge blocking resistance.¹⁰ Upon the curing reaction the TPD molecules dispersed in the mixture precursor film undergo a phase segregation process to make bigger aggregates (domains) (see Figure 3(c)), of which nanomorphology secures the charge percolation paths. In particular, the decreased thickness of MDPN nanolayer delivers the possibly reduced distance between these TPD aggregates during the segregation process, which improves the hopping charge (hole) transport between the TPD aggregates. As a consequence, the charge transport (hole mobility) of the MDPN nanolayer could be enhanced leading to the reduced threshold voltage.

The similar shift was observed for the turn-on voltage in the L-V characteristics (see Figure 2(b)). However, the uncured device shows relatively better up-turn shape for the luminance than the current density in contrast to the almost same trend for the cured device. This indicates that the uncured device is more efficient than the cured device as seen from the relative current efficiency trend (see Figure 2(c)): We note that despite the significantly reduced turn-on voltage the power efficiency was also lower for the cured device than the uncured device owing to the dominant role of higher current density for the cured device. This lower efficiency of the cured device can be attributed to the shifted emission (electron-hole recombination) zone toward the cathode (Al) side because the hole mobility of the MDPN nanolayer in the cured device was greatly improved upon the crosslinking reaction so that the majority of hole carriers was transported too far from the ideal emission zone (i.e., from the middle of Alq₃ layer in order to prevent possible quenching losses by the cathode or the MDPN layer). Owing to this shift of emission zone, the electroluminescence spectrum of the cured device was slightly red shifted from that of the uncured device. Here the major reason for this red shifted spectrum is probably attributed to the formation of slightly narrower or deformed gap (exciton) states than the pristine Alq₃ primary excitons due to the strong negative potential in the vicinity of the cathode (we note that a yellowish green electroluminescence was occasionally observed in case of poorly balanced OLED having the Alq₃ emission layer under high electric field¹¹), even though the optical cavity effect by the reduced thickness of whole active layer cannot be ruled out.

In summary, the molecularly doped polymeric network (MDPN) nanolayers were made by the thermo-chemical crosslinking (curing) reaction. The threshold and turn-on voltages were remarkably reduced for the OLED with the cured MDPN nanolayer, which is partially due to the thickness shrinkage by 29% during the curing reaction. In a microscopic viewpoint the reduced voltages are mainly

attributed to the improved charge (hole) carrier mobility owing to the charge percolation nanomorphology made by phase segregation process as well as the narrowed gap distance (thickness direction) between the TPD aggregates by the shrinkage during the curing reaction. However, considering the reduced efficiency of the cured device, the thickness control of MDPN nanolayers is of utmost importance to further enhance the device performance. Finally, the reliability of improved devices will be reported elsewhere, along with more detailed experimental data including further characterization of the crosslinking reaction of novolaks and evidence of the charge percolation nanomorphology, etc. Anyhow, the present result is expected to provide very useful guideline for improving the reliability of various types of OLEDs.¹²

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