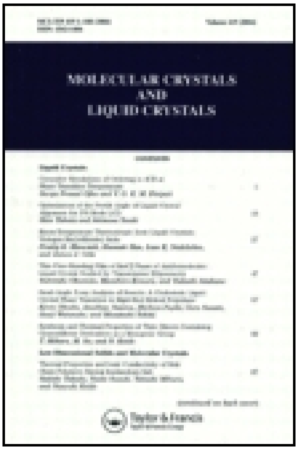

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Fabrication and Characteristics of Self-Assembled Monolayer of Oligophenylene Ethylene and Its Application in OLEDs

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Fabrication and Characteristics of Self-Assembled Monolayer of Oligophenylene Ethylene and Its Application in OLEDs

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We have synthesized 4-[(4-nitrophenyl)ethynyl]benzoic acid (NPBA) as a hole injection material for the modification of ITO surface and fabricated OLEDs consisting of ITO/NPBA self-assembled monolayer (SAM)/TPD (600 Å)/Alq_3 (600 Å)/Al (600 Å). The effects of ITO modified with NPBA SAM exhibited lower driving voltage than the device using 4-nitrobenzoic acid (NBA). Also, we have examined the interface properties between the modified ITO and adjacent organic layer from the measurements of contact angle and atomic force microscopy (AFM).

Keywords: 4-[(4-nitrophenyl)ethynyl]benzoic acid (NPBA); interface property; ITO, organic light emitting diode; self-assembled monolayer

INTRODUCTION

Indium tin oxide (ITO) has been commonly used as an anode of organic light emitting diode (OLED) because of relatively high work function, high transmittance and low resistance. However, poor interface property between ITO and adjacent organic layer limits hole injection from the anode electrode [1–2]. Many research groups have proposed a variety of method to facilitate hole injection into the organic layer such as surface treatments using specific acid/base solution [3], plasma or ozone treatment [4] and modification using self-assembled

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monolayer [5–7]. M. Carrara *et al.* [8] has demonstrated that it is possible to induce work function shift of ITO electrode by interface treatment with grafting dipolar molecules. Furthermore, they have reported that 4-nitrobenzoic acid (NBA) is the most proper candidate material for hole injection among para-substituted benzoic acid derivatives grafted on ITO. It is well known that carboxylic acids are promising attachment group onto indium tin oxide. In the present work, we have synthesized 4-[(4-nitrophenyl)ethynyl]benzoic acid (NPBA) as a novel hole injection material containing conjugated structure. ITO modified with NPBA self-assembled monolayer plays a role in the improvement of interface properties between ITO and adjacent organic layer because of high dipole moment, hydrophobicity, good adhesion and low resistance etc. Especially, the effects of NPBA conjugated backbone structure on the performance of OLED consisting of ITO/NPBA SAM/TPD (600 Å)/Alq_3 (600 Å)/Al were studied.

EXPERIMENTAL

Figure 1 shows the synthetic routes of NPBA compound. A solution of 1-ethynyl-4-nitrobenzene (1.5 g, 10.2 mmol), methyl 4-iodobenzoate (2.67 g, 10.2 mmol), dichlorobis(triphenylphosphine)palladium(II) (720 mg, 1.2 mmol), triphenylphosphine (270 mg, 1.2 mmol), CuI (200 mg) in TEA/THF (9:1 v/v, 100 ml) was thoroughly degassed using a stream of dry N_2, and then stirred vigorously under reflux at 50°C. After 24 h, the solution was concentrated and the residue was purified by column chromatography using methylenechloride and hexane, giving methyl 4-(2-(4-nitrophenyl)ethynyl)benzoate as a white solid (2.65 g, 91%). ^{1}H-NMR (500 MHz, D_6-DMSO); 8.297(d, J = 8.0, 2H);

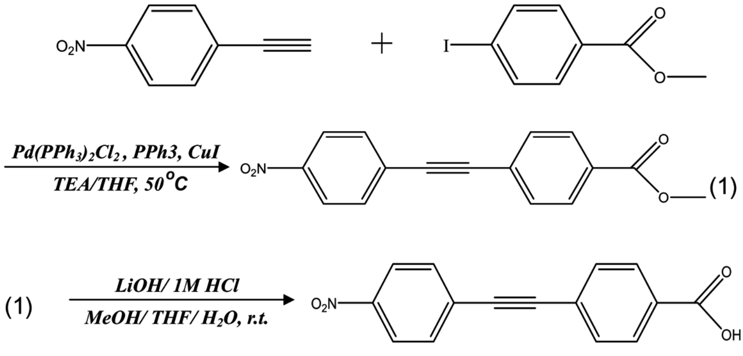

FIGURE 1 Synthetic routes of NPBA compound.

8.031(d, J = 8.0, 2H); 7.878(d, J = 8.0, 2H); 7.780(d, J = 8.0, 2H); Composition found: C, 68.01%; H, 3.97%; N, 4.80%. Calcd. C, 68.32%; H, 3.94%; N, 4.98%. Carboxylate (1) (500 mg, 1.8 mmol) and lithium hydroxide (247 mg, 10.7 mmol) solution in THF (80 ml), methanol (25 ml), and water (25 ml) were stirred at room temperature for 15 h. The mixture was acidified with 1 M HCl solution. The NPBA compound was obtained by filtration and drying under vacuum (yield 80%, white solid). ^{1}H-NMR (500 MHz, D_6-DMSO); 13.232(s, 1H, COOH); 8.283(d, J = 8.0, 2H); 8.000(d, J = 8.0, 2H); 7.861(d, J = 8.0, 2H); 7.740(d, J = 8.0, 2H); Composition found: C, 67.41%; H, 3.41%; N, 5.14%. Calcd. C, 67.42%; H, 3.39%; N, 5.24%. ITO glass ($\leq 12\Omega/\square$, 20 × 20 mm slides) was purchased from Shinan SNP Co. Each slide was cleaned by deionized water, followed by a sequence of ultrasonic bath in acetone and methanol for 60 min. The cleaned ITO substrates were immersed into the grafting solutions of NBA and NPBA, respectively. Solute concentrations were 1 mM in THF. After the grafting time of 15 h, the samples were rinsed in pure THF to remove excess molecules from the grafted surface. These substrates were used for contact angle measurement and transferred to thermal evaporator for device fabrication. The hole-only device and bilayer OLED were fabricated by high-vacuum (10^{-6} Torr) thermal evaporation onto ITO substrates containing each grafting molecules. For the hole-only device, a hole transport layer of N-N′-diphenyl-N,N′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD, 1500 Å) and an aluminum cathode (500 Å) were deposited sequentially. For the bilayer OLED, a TPD layer (600 Å) was deposited on ITO anode, followed by a light-emitting layer of tris-(8-hydroxyquinoline) aluminum (Alq_3, 600 Å) and an aluminum cathode (600 Å). Current density-voltage characteristics were measured using sourcemeter (KEITHLEY-2400). Finally, ITO substrate with a TPD layer (50 Å) was fabricated and surface morphology was investigated with atomic force microscopy (AFM, Autoprobe CP, PSI, USA) in non-contact mode at room temperature. AFM images were obtained at a scan rate of 1.0 Hz with a silicon cantilever (Ultralever 06B, PSI, USA).

RESULTS AND DISCUSSION

The head group, carboxylic acid, of NBA and NPBA has a high affinity for the surface OH group of ITO, which facilitates chemisorption of the self-assembly molecules onto the ITO substrate. The results of contact angle measurements of self-assembly molecules indicated that the change of body group reduces the wettability and surface energy as shown in Table 1. The contact angle of bare ITO is 31°, which can be

TABLE 1 Calculated Surface Energy of ITO Modified with NBA and NPBA by Owens-Wendt Geometric Means

[1] Anode	[1] Water [2] (± 1°)	[1] Formamide [2] (± 1°)	[1] γ_s^p [2] (mJ/m^2)	[1] γ [2] (mJ/m^2)
[2] NBA-assembled ITO	[3] 41	[3] 28	[2] 35.3	[3] 56.4
[3] NPBA-assembled ITO	[4] 48	[4] 31	[3] 27.9	[4] 52.3

$^*\gamma_s^p$: polar component, γ: surface energy, the sum of polar and dispersive component.

attributed to the OH group remaining on surface [9]. It can be found that the difference of surface energy for the self-assembly molecules via Owen-Wendt geometric method [10] is mainly due to the polar components.

Relatively low polar component of NPBA-assembled ITO improved the compatibility between ITO electrode and TPD layer. The topographical images of TPD films (3 μ × 3 μ area, 50 Å) on bare ITO, NBA-assembled ITO and NPBA-assembled ITO (Fig. 2a, b and c, respectively). NPBA-assembled ITO has a well-dispersed TPD layer compared to the NBA-assembled ITO, which is caused to the high hydrophobic property and compatibility for TPD molecules. Also, the morphology of TPD layer onto the NPBA-assembled ITO shows dense and large grain domain compared to TPD layer onto the NBA-assembled ITO, implying that NPBA molecules is well- ordered owing to the rigid and bulky backbone structure of oligophenylethynylene. In order to explore the effects of ITO modification using the SAMs on the electrical properties of organic devices, the hole-only devices (ITO modified with SAMs/TPD (1500 Å)/Al) and the typical OLEDs (ITO modified with SAMs/TPD (600 Å)/Alq$_3$ (600 Å)/Al) were fabricated. The effects of the SAMs modified ITO on the hole injection efficiency were investigated. Figure 3 showed the current density-voltage characteristics of the hole-only device. The drive voltage of the NPBA-assembled device was decreased, which is mainly due to the decrease

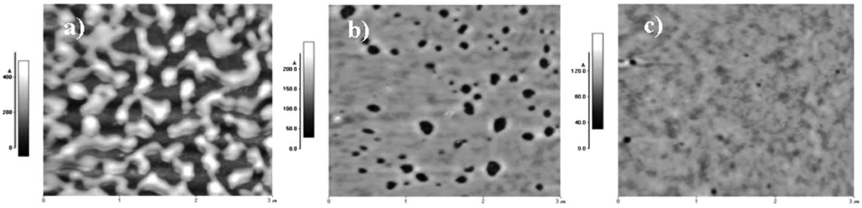

FIGURE 2 AFM images for TPD film (50 Å) on bare ITO (a), NBA-assembled ITO (b) and on NPBA-assembled ITO (c).

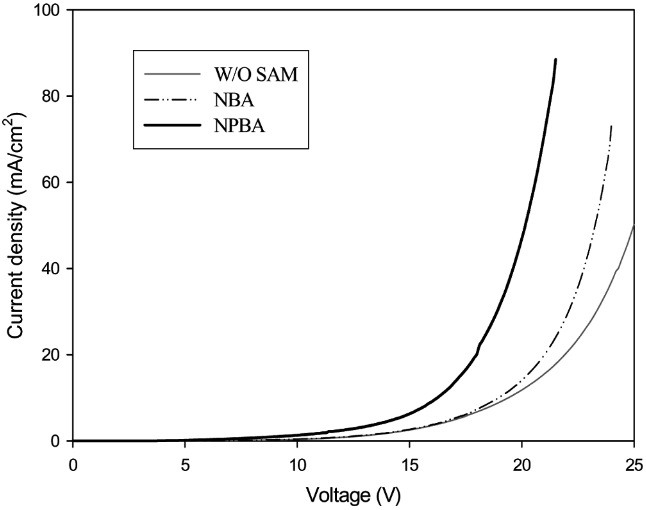

FIGURE 3 Current density-voltage characteristics of the hole-only devices consisting of SAMs modified ITO/TPD (1500 Å)/Al (500 Å).

of energy barrier for hole injection because of the high dipole moment of NO_2 group and the low electrical resistance. Also, it may be attributed to the good adhesion property for the interface between ITO anode and TPD layer because of the high hydrophobic property. It

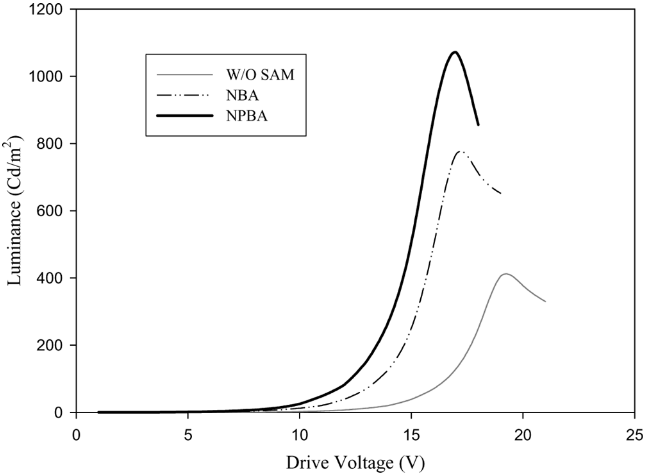

FIGURE 4 Luminance-voltage characteristics of OLEDs consisting of SAMs modified ITO/TPD (600 Å)/Alq_3 (600 Å)/Al (600 Å).

can be concluded that the hole-only device consisting of NPBA-assembled ITO/TPD/Al exhibited low drive voltage, implies that the prepared device has many active-sites for charge transfer owing to the well-dispersed TPD layer onto the NPBA-assembled ITO substrate. Figure 4 showed the luminance-voltage characteristics of bilayer OLEDs. It should be noted that OLED using NPBA-assembled ITO showed maximum luminance of 1,070 cd/m^2 at 17 V. This is attributed to the improvement of interface between ITO anode and TPD layer.

CONCLUSIONS

Surface modification of ITO with functional SAMs has already known as a good candidate to improve the performances of organic devices. NPBA compound having oligophenylene ethylene moiety in the backbone structure was synthesized as a novel surface modifier of ITO. The conjugated structure of NPBA results in the facilitation of hole carrier injection owing to the improvement of hydrophobicity, adhesion and electrical property. Thus, OLEDs using the NPBA-assembled ITO showed relatively low drive voltage and high luminance.

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