Charge-Transporting Property of Polymer Films Doped with Organic Stable Radicals

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Keywords: organic light-emitting-diode, stable radical, hole-transporting, radical dopant

1. Introduction

Organic light-emitting-diodes (OLEDs) have been developed for applications in a flat panel display[1]. Because the emission mechanism of the OLED is based on the recombination process of holes and electrons injected from the electrodes, the performance of the device is significantly influenced by the energy barrier at the interfaces and the balance of charges. Since Tang et al.[2] demonstrated the effectiveness of the hole transporting layer for improvement of device efficiency, various hole transporting materials have been eagerly studied. A hole or electron is transported by hopping on the highest occupied molecular orbitals (HOMOs) or the lowest unoccupied molecular orbitals (LUMOs) (Figure 1a, b). It is reported that the hole transporting property of aromatic amine polymers is improved by doping with an organic radical oxidant, tris(*p*-bromophenyl) aminium hexachloroantimonate **1** [3, 4]. However, to the best of our knowledge, there has been no report on hole transport in amorphous organic radical molecules having singly occupied

molecular orbitals (SOMOs), as shown in Figures 1c, and d. If charges are transported by the hopping on SOMOs of open-shell molecules, it would give not only a novel hopping diagram but also the possibility to develop a conducting system in which charge transporting is modulated by external stimuli such as a magnetic field.

In this study, we prepared three kinds of organic stable radicals, and studied their charge transporting properties.

2. Experimental

Tris(*p*-bromophenyl)amine (TBA), the galvinoxyl radical **2**, and di(*p*-anisyl)nitroxide **3** were prepared according to the literature[5, 6]. The aminium radical **1** was purchased from the Aldrich Co. and used without further purification. The radicals and TBA were resolved in dichloromethane or 1, 2-dichloroethane solutions of poly-

Figure 1. Schematic diagrams of hopping conduction.

Figure 2. Chemical structures of organic stable radicals.

Figure 3. Current density-electric field characteristics of the PC films doped with 1-3 (a) and with 1-3 and TBA (b)-(d); total concn of the radical and TBA = 16 mM.

(bisphenol A carbonate) (PC) (10 g/l). The solution was spincoated on an ITO (indium tin oxide) glass substrate, and aluminum was evaporated onto it as the cathode.

3. Results and Discussion

The current density vs the electric field characteristics of the PC films doped with the radicals are shown in Figure 3a. The nitroxide 3 doped film showed a higher charge transporting ability compared with the films of galvinoxyl 2 or the aminium radical 1. For an efficient charge transport, the small energy gap on the surface of the electrode and a large carrier mobility in the charge transporting layer are important, but 1 and 2 have high ionization potentials, I_p , and an extremely low carrier mobility. Meanwhile, 3 has a low I_p of 4.9 eV estimated by cyclic voltammetry. Hence, although the current density of 3 is low because of its low drift mobility, the hole injection at a low driving voltage is more efficient than that of TBA (I_p = 5.6 eV), these results suggest the possibility of charge injection with organic radicals

the using SOMO's redox.

The current density of TBA with each radical is shown in Figures 3b, c and d. The highest current density was observed when the ratio of the radical and TBA was 2/8 (1 / TBA), 2/8 (2 / TBA), and 0/10 (3 / TBA), respectively. We considered that 1 and 2 have a p -dopant ability to increase the carrier density, but the nitroxide 3 acts as a hole trapping site to decrease the carrier mobility.

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