Review

Organic materials for organic electronic devices

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ABSTRACT

In recent years, organic electronic devices which use organic materials as an active layer have gained considerable interest as light-emitting devices, energy converting devices and switching devices in many applications. In these organic electronic devices, the organic materials play a key role of managing the device performances and various organic materials have been developed to improve the device performances of organic electronic devices. In this paper, recent developments of organic electronic materials for organic light-emitting diodes and organic solar cells were reviewed.

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1. Introduction

Organic electronic devices are differentiated from inorganic electronic devices in that organic materials are used as active materials in the devices. The use of organic materials instead of traditional inorganic materials gives many advantages such as simple processing, low cost manufacturing, versatile molecular design and easy control of physical properties of materials. Therefore, several organic electronic devices have been developed, which include organic light-emitting diodes (OLEDs) [1–7], organic solar cells (OSCs) [8–34], organic thin film transistor [35,36] and organic bistable memory devices [37–46]. Among these devices, OLEDs and OSCs are the most actively studied organic electronic devices.

The OLEDs have been developed for more than 20 years and are being used as a display for mobile phones and TVs. The OLEDs convert electric energy to photon energy and have a device structure with multilayer organic materials sandwiched between two electrodes. Indium tin oxide (ITO) has been typically used as the anode and hole injection layer, hole transport layer, emitting layer and electron transport layer were stacked on the ITO followed by cathode deposition on the electron transport layer. In general, light-emitting properties of OLEDs are dominated by light-emitting materials, but other charge transport materials are also critical to the device performances of OLEDs because driving voltage and quantum efficiency are affected by the charge transport layer. Therefore, charge transport materials and light-emitting materials are two types of important materials for OLEDs.

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OSCs convert solar energy to electrical energy by absorbing sunlight. The OSCs have a device structure with a hole collection layer, a light absorbing layer and a cathode stacked on an anode. Typically, ITO has been used as the transparent anode and organic materials were stacked on the ITO by solution or vacuum coating process. The device performances of OSCs are mostly dependent on the light absorption by the light absorbing organic materials and other organic materials aids charge collection at the electrodes. Therefore, most researches on OSCs have been devoted to develop good light absorbing materials for OSCs.

In this work, we reviewed recent developments of organic materials for OLEDs and OSCs. Charge transport materials and light emitting materials of OLEDs and light absorbing materials of OSCs were summarized in this work. We also proposed future direction for the development of organic materials for OLEDs and OSCs.

2. Organic light-emitting diodes

The phenomenon of organic electroluminescence was first discovered by Pope et al. using anthracene single crystals [47]. Since the OLED device based single crystal of anthracene was very thick and worked at very high voltages, the device was not commercialized.

Tang and VanSlyke of Eastman Kodak have demonstrated a highly efficient multi-layer OLED known as today's OLED technology [48]. OLED device by Tang and VanSlyke was based on bilayer organic structure. Quantum efficiency and power efficiency of 1% and 0.46 m/W were reported and this work has stimulated a very intense activity in the field of OLEDs.

Since the discovery of bilayer OLED structure by Tang and VanSlyke, more organic layers have been used with specialized functions such as the hole injecting layer, hole transporting layer, hole blocking layer and electron transporting layer. It has been shown that the electroluminescence efficiency of OLEDs can be increased by carrier or exciton confinement within a multilayer device. Therefore, the development of materials with characteristics that are optimized for each layer is an important for OLED development.

2.1. Charge transport materials

2.1.1. HIL materials
Treatment of the anode (mainly ITO) by O_2 plasma or ultraviolet-ozone can increase its work function up to near 5.0 eV. However, the carrier injection energy barrier from ITO to the highest occupied molecular orbital (HOMO) of common hole-transport materials is around 0.5 eV, which limits the hole injection from ITO to the hole transport materials. A hole injection layer (HIL) material which reduces the energy barrier between anode/hole transport layer (HTL) is therefore beneficial to enhancing charge injection at the interfaces and ultimately improving power efficiency of the device. Generally, a HIL material used in OLED device was required to possess the following properties; (1) suitable HOMO level between the work function of the ITO and the HOMO of HTL materials; (2) high thermal stability with high glass transition temperatures; (3) smoothening effect of relatively rough ITO surface; (4) transparent in the red, green and blue (RGB) wavelength region. These properties of hole-injection material in OLED device are critical to the power efficiency and lifetime. Conventional HIL materials such as copper phthalocyanine (CuPc) and poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT/PSS) were typically used in OLEDs (Fig. 1) [49,50]. CuPc showed good surface and thermal properties, but had a problem of light absorption in red and blue wavelength region.

PEDOT/PSS is one of the widely used polymers for HIL for both polymer light-emitting diodes (PLEDs) and small-molecule OLEDs. The aqueous gel dispersion of PEDOT/PSS as hole injection layer can form a uniform, conductive, and transparent thin film, which can smooth the surface of ITO anode, enhance the adhesion to the organic layer, and decrease the hole injection barrier due to its low HOMO level (5.1 ± 0.1 eV). Therefore, PEDOT/PSS can reduce the turn-on voltage and prolong the lifetime of the device.

Aryl amine type HIL materials are among the most widely investigated electron transport materials for OLEDs. The most well-known aryl amine is 4,4′,4″-tris-(N-(naphthalen-2-yl)-N-)triphenylamine (2-TNATA), 4,4′,4″-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA) (Fig. 1) [51]. Especially, m-MTDATA showed good device performances as the HIL between the ITO anode and HTL. Main mechanisms for these property improvements were dense film structure and fine surface morphology which lead to easier hole migration at the ITO/HIL and HIL/HTL junctions. However, HIL materials based on aryl amine had the disadvantage of a low glass transition temperature (T_g) (i.e. T_g of m-MTDATA is 77 °C).

Recently, HIL materials for OLEDs based on phenoxazine with high thermal stability were reported (Fig. 2) [52]. 10,10′-bis(4-tert-butylphenyl)-N7,N7′-di(naphthalen-1-yl)-N7,N7′-diphenyl-10H,10′H-3,3′-biphenoxazine-7,7′-diamine (1-PNA-BPBPOX) showed high T_g of 161 °C, which was higher than that of a aryl amine type HIL material. Also, the HOMO level of 1-PNA-BPBPOX was −4.86 eV, indicating a good match between the work function of ITO and the HOMO (about −5.4 eV) of a common hole transporting materials. The 1-PNA-BPBPOX was used as the HIL in OLED devices, yielding power efficiencies of 2.8 lm/W. 1-PNA-BPBPOX yields a higher power efficiency, by a factor of 33%, than the 2-TNATA. Also, OLED device containing 1-PNA-BPBPOX exhibited a longer device lifetime than 2-TNATA.

2.1.2. HTL materials
The important properties of HTL materials include the following; (1) Suitable HOMO and LUMO level for efficient charge injection to achieve a low driving voltage and electron blocking. (2) Stability to electrochemical oxidation with a high oxidation potential. (3) High glass transition temperature to prevent recrystallization during device operation. (4) High hole mobility. (5) In phosphorescent OLED device, triplet energy higher than that of host material to confine triplet exciton within the emitting layer.

In general, aryl amine and carbazole derivatives containing nitrogen atom have been developed as the HTL materials, due to the electron-donating capabilities. Typical HTL materials such as N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzidine (TPD) and N,N′-di-[(1-naphthyl)-N,N′-diphenyl]-1,1′-biphenyl)-4,4′-diamine (α-NPD) have aryl amine units attached to biphenyl backbone [49,53]. The HOMO and LUMO of TPD are −5.4 and −2.4 eV and α-NPD has the same energy levels as TPD. In addition, hole mobility of TPD and α-NPD is known to be as high as 1.1×10^{-3} cm^2/V s. However, TPD and α-NPD have relatively low T_g of 65 °C and 95 °C, respectively. HTL materials with low T_gs cause the crystallization by Joule heating during device operation and increase the device temperature. Therefore, the development of HTL materials was directed to increase the T_gs of HTL materials.

4,4-Bis(N-iminostilbenyl)biphenyl (ISB), N,N′-di(biphenyl-4-yl)-N,N′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (p-BPD) and N,N′-di(naphthalene-1-yl)-N,N′-di(phenanthren-9-yl)-biphenyl-4,4′-diamine (NPhenD) were reported as high T_g HTL materials with a biphenyl backbone structure [54–56]. The chemical structures of ISB, p-BPB and NPhenD are shown in Fig. 3.

These materials have high T_g (115 °C for ISB, 102 °C for p-BPD, 195 °C for NPhenD) and moderate hole mobilities. The hole mobility of NPhenD under an electric field of 0.2 MV/cm at room