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NONPLANAR AND BRANCHED ELECTRON TRANSPORTING MOLECULES FOR ORGANIC EL DEVICE

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Abstract Novel nonplanar and branched electron transporting molecules which exhibit stable amorphous glassy state and high solubility into the polymer matrix have been synthesized and applied to the molecularly doped polymer EL device.

INTRODUCTION

Organic electroluminescent (EL) devices based on molecularly doped polymer (MDP) have been studied extensively for display applications because of their high possibility to large-area light emitting displays [1]. For example, the EL devices fabricated with poly (N-vinylcarbazole) (PVK) as a hole transporting polymer matrix, oxadiazole derivatives such as 2-(4'-tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxadiazole (PBD) or 2,5-bis(1-naphtyl)-1,3,4-oxadiazole (BND) as an electron transporting molecule and coumarin 7 as an emitting molecule were successfully demonstrated [2]. The excellent electron transporting ability of the PBD and BND based on oxadiazole moiety has been

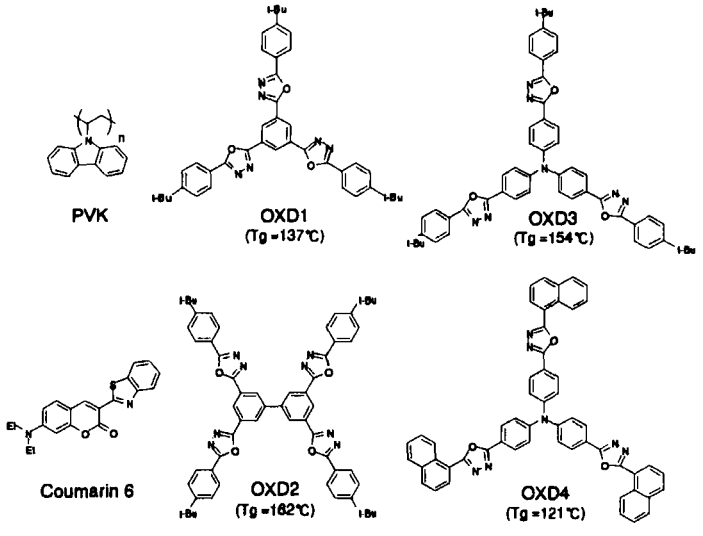


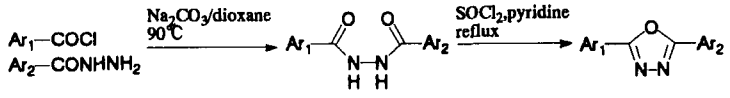
FIGURE 1 Molecular structures of hole transporting polymer, emitting molecule and synthesized electron transporting molecules.

reported previously [3]. It is known that the luminous efficiency increases with increasing the concentration of the electron transporting molecule. However, it is difficult to disperse the electron transporting molecules in high concentration into the polymer matrix because of their crystallization in the matrix. One of the approaches to this problem is covalent linkage of electron transporting molecules to the polymer back born. However, a disadvantage of the polymers is the difficulty of removal of by-product incorporated into the polymer during the polymerization process. Another approach is utilizing a low molecular weight compound which forms stable amorphous glassy state and has high solubility into the polymer matrix. An advantage of this method is that they can be purified easily by chromatography, recrystallization or sublimation. To obtain such compounds, we have designed novel molecular structures based on oxadiazole moiety, having nonplanarity and branch, to improve the solubility, because the low solubility of PBD and BND is attributable to the linear and planar shapes of the molecules. Such structures would be expected to cause the disorder of intermolecular orientation and lead to the stable amorphous glassy state. In this paper, we present the synthesis of novel electron transporting materials and EL characteristics of the MDP EL devices.

EXPERIMENTAL

The oxadiazole derivatives, synthesized in this study, with branch structure (OXD1, OXD2) and nonplanar structure (OXD3, OXD4) are shown in FIGURE 1. The OXD1 has three limbs and the OXD2 has four limbs. The OXD3 and the OXD4 are nonplanar because of the triphenylamine moiety; three phenyl groups attached to the nitrogen atom of the triphenylamine cannot be in the same plane for the steric repulsion. Oxadiazole ring unit was synthesized by the cyclization of corresponding bis(aryl)hydrazines in thionyl chloride and pyridine (SCHEME1). Unsymmetric bis(aryl)hydrazines were prepared from corresponding aryl acylhalides and monoarylhydrazines (FIGURE 2, TABLE1).

The OXDs were used as electron transporting materials for MDP EL device. The device structure in this study was ITO/organic layer/Mg:Ag (FIGURE 3). The sheet resistance of the ITO (indium tin oxide) was 15Ω/□ and the thickness of the Mg:Ag (10:1) top electrode was 180nm. The organic layer consists of PVK as the hole transporting polymer, oxadiazole derivatives (OXDs) as the electron transporting molecules and coumarin 6 as the emitting molecule, (50:49:1 wt%, respectively). The organic layers of 100 nm thickness were dip-coated onto the ITO-coated glass substrate from dichloroethane solution. Uniform organic layers were obtained by the dip-coating.



SCHEME 1 Synthetic scheme of oxadiazole ring

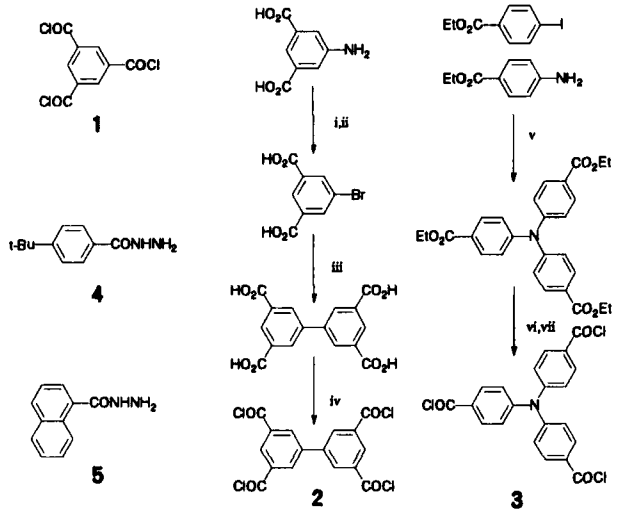


FIGURE 2 Precursors of OXDs, and their synthetic scheme. i, HBr, $NaNO_2$; ii, CuBr (85%); iii, $PdCl_2$•2NaCl, HCO_2H, MeOH (10%); iv, $SOCl_2$, DMF (95%); v, Cu, K_2CO_3, xylene (80%); vi, KOH, EtOH (92%); vii, $SOCl_2$, DMF (95%)

TABLE 1 Synthesis of OXDs from precursors

oxadiazole	precursor		yield%
	Ar_1—COCl	Ar_2—$CONHNH_2$	
OXD1	**1**	**4**	**34**
OXD2	**2**	**4**	**43**
OXD3	**3**	**4**	**93**
OXD4	**3**	**5**	**96**

RESULTS AND DISCUSSION

From differential scanning calorimetry (DSC) measurements, we found that these derivatives have high glass transition temperatures; 137 °C for OXD1, 162 °C for OXD2, 154 °C for OXD3, 121 °C for OXD4. Scanning rate was 10°C/min. Exothermic peak attributable to the crystallization was not observed in the range of 25-300°C.

The OXDs were dispersed into the PVK matrix. Smooth and amorphous films were obtained by the casting from chloroform solution of OXDs and PVK (50:50 wt%). Even in the high concentration of OXDs, no crystallization and phase separation of

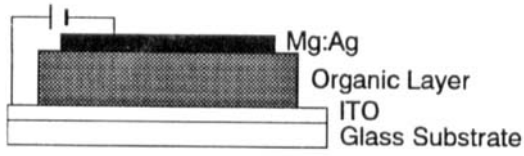


FIGURE 3 Configuration of the MDP EL device.

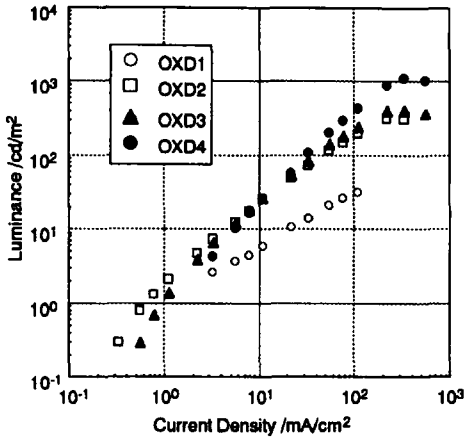


FIGURE 4 Luminance-current density characteristics of the MDP EL devices with OXDs as the electron transporting molecules.

these molecules was confirmed from DSC measurements and optical microscopic observation. Such excellent dispersion stability is attributable to the existence of branch and nonplanar structure in the molecules.

All the EL devices emitted green light which corresponds to the photoluminescence spectrum of coumarin 6. FIGURE 4 shows the luminance-current density characteristics for the EL devices with OXDs . The EL efficiencies at 10mA/cm^2 were comparable except for the device with OXD1. Maximum luminance of 1040cd/m^2 was obtained in the device with OXD4 at 14V. The luminous efficiency at 100cd/m^2 was about 0.12 lm/W. Turn-on voltages for light emission of the devices with OXD1, OXD2, OXD3 and OXD4 were 6.5V, 8V, 8V and 4.5V, respectively. The lowest turn-on voltage was obtained in the OXD4 doped EL device. It can be explained by lower reduction potential of OXD4 having naphtyl group than OXD3 having phenyl group.

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