Electron and Hole Mobility in Vacuum Deposited Organic Thin Films of Bis[2-(2-hydroxyphenyl)benzoxazolate]zinc and Its Derivatives

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The electronic properties of five derivatives of bis[2-(2-hydroxyphenyl)benzoxazolate]zinc (ZnPBO) have been investigated by the time-of-flight measurement of their thin films prepared with vacuum deposition. The electron and hole mobilities at electric field of 5×10^5 V/cm for these compounds were 10^{-5} cm²/Vs and 10^{-6}-10^{-8} cm²/Vs, respectively. The electron mobility was found to be almost identical among those used in this study and higher than that of the representative electron transporting organic material, Alq. The hole mobility had significantly increased as the π-conjugation of the ligands of the complexes was extended.

For an organic light emitting diodes (OLEDs), an amorphous thin film of an organic semiconductor is generally used. However, the charge carrier mobility of such a film is known to be quite low. For example, the typical hole transport material, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) shows the hole mobility at around 10^{-3} cm²/Vs.[1] Moreover, one of the representative electron transport materials, tris(8-hydroxyquinoline)aluminum (Alq), shows the electron mobility of the order of 10^{-6} cm²/Vs.[2] It is, therefore, the most important issue for the performance of OLEDs to improve the carrier balance and driving voltage by developing electron transport materials with high electron mobility.[3]

Recently, relatively high electron mobility of several organic materials was reported.[4] However, the authors described little systematic data relating to the electronic transport properties of organic semiconductors with the molecular structures. In the present study, we investigated the electron and hole mobility using the time-of-flight (TOF) technique[5] in vacuum deposited films of Zn-complexes containing a series of 2-(2-hydroxyphenyl)benzoxazolate (PBO) derivatives as a ligand.
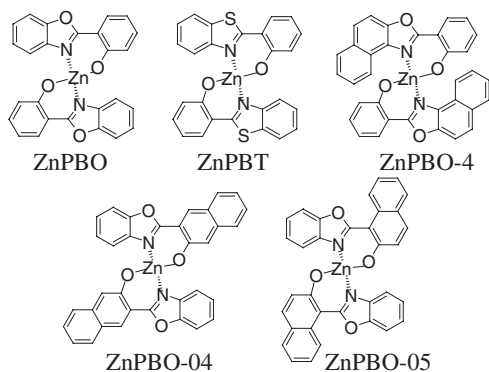

Figure 1. Chemical structures used in this study.

We synthesized the four kinds of the PBO derivatives and their Zn-complexes shown in Figure 1. The oxygen atom of the benzoxazole in PBO was substituted by a sulfur atom in PBT. A naphtyl group was introduced to PBO-4, PBO-04 and PBO-05 instead of the phenyl group in PBO. The synthesis of PBO-05 was as follows. Twenty gram of P_2O_5 was added into 200 g of CH_3SO_3H little by little with vigorous stirring. After the turbid mixture became clear, unit mole of 2-hydroxy-1-naphthoic acid was added gradually into the mixture and then one mole of o-aminophenol was added, followed by mild stirring at 100 °C for 3 h. The reaction mixture was poured into ice water. The resulted precipitate was collected by filtration and dissolved again in chloroform. After filtering the insoluble, the filtrate was solidified upon solvent evaporation. The other derivatives were synthesized with similar procedure but the reactants were varied upon desired products. Complexation of the PBO derivatives was performed according to the known procedure,[6] followed by train sublimation method before use.

ZnPBO has been reported to be useful for a blue emission material in double-layer EL devices.[6] The luminance characteristics of the Zn-complexes have been described elsewhere.[7] They show various color from blue to yellow depending on the ligand structures. Especially, ZnPBT was proposed to be used for a single-component white-emitter.[8] The samples for the time-of-flight measurement were prepared as follows. A semitransparent aluminum electrode was vacuum deposited on a glass substrate through a stripe metal mask with the thickness of 20 nm and the width of 2 mm. On the top of the substrate, Zn-complexes were vapor deposited at a rate between 2 and 4 nm/s. A counter electrode of 40 nm aluminum film was deposited on the top of the organic layer through the same metal mask vertically set to the stripe of the first electrode. The sample area was 2×2 mm². The thickness of Zn-complex films was determined with a Sloan Dektak 3 profilometer to be ranged between 3.4 and 6.9 μm. During all the evaporation process, the background pressure was kept at 2×10^{-6} torr. A N₂ laser with a pulse width of 3 ns at a wavelength of 337 nm was used for irradiation. ZnPBO derivatives have strong absorption at 337 nm. Approximately 90% of irradiation light should be absorbed within 270 nm from Al electrode in the ZnPBO film. A thin sheet of charge carriers drifts across the film under the influence of an externally applied bias voltage and an abrupt drop in current indicates the arrival of the carrier sheet at the exit contact. Selection of a sense of the bias voltage allows electron and hole transients to be independently studied. Transient currents were monitored as a voltage change across the load resister (1 kΩ to 10 kΩ for electrons, 500 kΩ to 1 MΩ for holes) with a digital storage oscilloscope. We observed time-resolved transient cur-
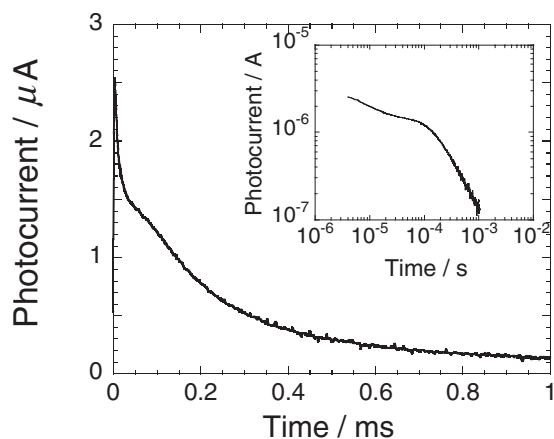
Figure 2. The transient photocurrent profile plotted in liner and both double logarithmic (inset). The photocurrent due to electron transport of ZnPBO recorded at an electric field 4.0×10^5 V/cm.

rents due to a displacement of a sheet of charge carriers that were generated in a Zn-complex layer close to an illuminated semitransparent electrode.

Figure 2 shows the transient photocurrent profiles for ZnPBO at room temperature. For a dispersive carrier transport observed in Figure 2, the transit time can be determined from double logarithmic plots according to the Scher–Montroll method.[9] A clear kink was found in the double logarithmic plot and a transit time was estimated from the intersection of the two slopes before and after the kink. The electron mobility of the Zn-complexes was plotted in Figure 3 as a function of a square root of the electric field at room temperature. The exponential square root of the electric field is that typically found for disordered organic systems from moderate to large electric field.[10] Electron mobility of each Zn-complex was found around 10^{-5} cm^2/Vs independent of the molecular structure at the moderate electric field of 5×10^5 V/cm. Figure 4 shows the hole mobility of the Zn-complexes. It is notable that both electron and hole mobilities were measurable and higher than those of Alq in one order of magnitude. Although significant correlation of the electron mobility with the molecular structure of Zn-com-
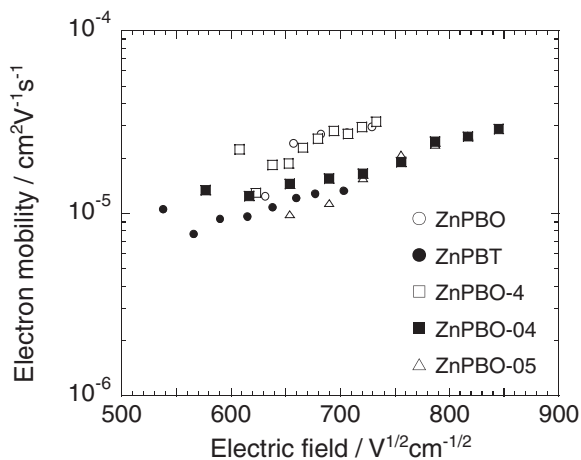

Figure 3. The electron mobility of the Zn-complexes plotted against the square root of electric field.
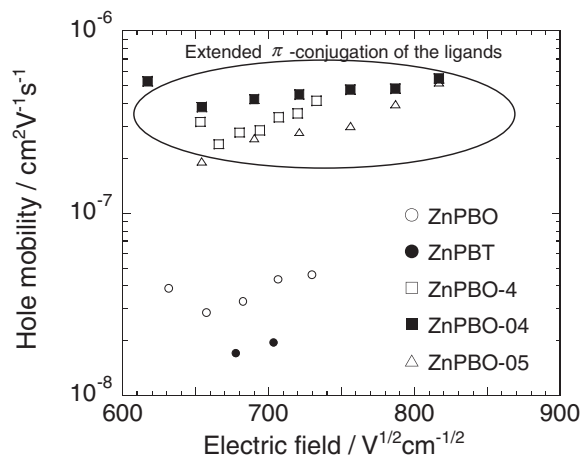

Figure 4. The hole mobility of the Zn-complexes plotted against the square root of electric field.

plex was not observed, the hole mobility was found to be increased as the extension of π-conjugation of the ligand. Since oxygen trap is known to be a dominant factor for electron transport property in many organic semiconductors,[11] it is understandable that the electron mobility is little affected by the structural difference. On the other hand, the hole mobility depended on the chemical structures probably due to the intermolecular packing effect in solid films.

We investigated the electron and hole mobility in vacuum deposited films of Zn-complexes using time-of-flight technique. The electron mobility of ZnPBO was found to be the highest among them. The value of 2.8×10^{-5} cm^2/Vs at electric field of 5×10^5 V/cm clearly indicates that ZnPBO is a superior electron transport material to Alq. In addition, the hole mobility was ranged between 10^{-8} and 10^{-6} cm^2/Vs, depending on the π-conjugation extent in the ligand. These findings may give a good guide for molecular design of carrier transport materials.

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