Electron transportation with mobility of above 10^{-3} cm²/Vs in amorphous film of co-planar bipyridyl-substituted oxadiazole

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We demonstrate that a bipyridyl substituted oxadiazole (Bpy-OXD) shows high electron mobility that reached above 10^{-3} cm²/Vs. We believe the high mobility results from both the hybrid molecular structure of the two electron-accepting units: bipyridyl and oxadiazole, and the planar molecular structure based on its no steric hindrance and no bulky substituent. The computational analysis elucidates that the amorphous nature of Bpy-OXD in thin-film state probably results from the polymorphic effect in isolate state and the volume effect in solid state.

Organic light-emitting devices (OLEDs) have received a lot of attention because of their potential applications in flat-panel displays and lighting. In general, OLEDs are composed of functionally divided multilayers such as hole injection, hole-transporting (HT), emissive, hole-blocking, electron-transporting (ET) layers, and so on. This structure enables the optimal charge balance essential to high electroluminescence (EL) efficiency.[1,2] In the last decade, many kinds of amorphous molecular semiconductor materials, working as HT materials and ET materials, have been proposed.[3,4]

Charge mobility in amorphous organic semiconductors is a crucial issue to enhance current *vs.* voltage characteristics of OLEDs, and high mobility leads to lower operation voltage and lower power consumption. Fast hole mobility up to almost 10^{-3} cm²/Vs in such materials has been already achieved, for example, those of N,N'-diphenyl N,N'-bis(m-toly)benzidine (TPD) and N,N'-dinaphthyl N,N'-diphenylbenzidine (NPB) reach almost 10^{-3} cm²/Vs.[5] On the other hand, electron-transporting in amorphous organic semiconductors for OLEDs still has some issues about mobility and trap density. In fact, Even in high performance silole base ET materials reported recently,[6] electron mobility is reported to be about 10^{-4} cm²/Vs[7] and still almost 1-fold lower than the hole mobilties. However, there is no principal reason about the low electron mobility in amorphous organic semiconductors excepting for external perturbations such as oxygen carrier traps. Actually, high field-effect electron mobility of 2.1 cm²/Vs has been reported in polycrystalline organic thin-film transistors,[8] and that is comparable with field-effect hole mobility of pentacene thin-films.

Strong electronic coupling between adjacent two molecules is crucial for charge carrier transport. In this mean, while needless to say that high electron affinity of molecules is important for ET, planar molecules with a large π-electron system are advantageous. On the other hand, such planar molecules result in (poly)crystalline thin-films not amorphous glass thin-films that are more suitable for OLED applications. In this paper, we demonstrate high electron mobility above 10^{-3} cm²/Vs in molecular amorphous films which are made of a planar organic compound previously reported as an excellent ET layer material for OLEDs. We also demonstrate a reason why the planar molecule possesses a good amorphous nature by means of computational chemistry.

Fig. 1(a) shows the molecular structure of the bipyridyl-substituted oxadiazole ET material abbreviated as Bpy-OXD, which was reported previously as an excellent ET layer material because of its high electron affinity based on the two electron-accepting unit hybridization.[9] As clearly shown in the figure, the molecule consists of planar ring units only. Therefore, strong electronic interactions among adjacent molecules can be supposed, resulting in high electron mobility.

Fig. 2 shows the transient photocurrent waveform under a 500-ps pulse light excitation by a N_2 gas laser (λ=337 nm). The inset of Fig. 3 shows the structure of the test device. The 100-nm-thick C_{60} layer was utilized as a charge carrier photogeneration layer, because the bandgap of Bpy-OXD is too wide (3.64 eV)[9] to efficiently absorb the excitation laser. The double logarithmic plot of the waveform presented as the inset of Fig. 2 showed a kink to indicate a charge carrier transit to the counter electrode. By using the following equation with the transit time (t_T), the applied voltage (V), the distance between the two electrodes (D), and the thickness of Bpy-OXD layer (d):

$$\mu = Dd/(t_T V) \tag{1},$$

the mobility (μ) was estimated to be 3.1×10^{-3} cm^2/Vs at the electric field ($E = V/D$) of 1.15 MV/cm. Although the transient photocurrent waveform is not clearly non-dispersive, the mobility value reached above 10^{-3} cm^2/Vs, which is among the highest values reported in the literature on ET materials for OLEDs. Note that while comparable electron mobility in amorphous solid films has been already obtained from novel oligofluorenes reported by Wu,[10] such materials have lower electron affinity,[11] resulting in difficulties of electron injection from cathode; the materials are probably not suitable as ET materials for OLEDs.

Fig. 3 shows electron mobility as a function of the square root of electric field for Bpy-OXD together for tris(8-qunolinato) aluminum (Alq),[7] the common ET material for OLEDs. As clearly shown in the figure, Bpy-OXD shows much higher mobility than Alq. The filed-dependence of the mobilities in Fig. 3 both follows the universal Poole-Frenkel relationship: $\mu \propto \exp(\beta E^{1/2})$, where β is the Poole-Frenkel factor.[12,13] Such relationship is often observed in disordered organic systems and could be attributed to effects of energetic and positional disorder on the hopping conduction in amorphous organic solids. The much small dependence for Bpy-OXD in contrast to Alq probably means small disorders on the charge hopping.

Next, we would like to discuss the origin of highly amorphous nature of Bpy-OXD that consisted of planar rings only. As shown in Fig. 1, Bpy-OXD will have crystallinity of high due to co-planar structures without any steric hindered substituents. On the contrary to such expectation, Bpy-OXD forms excellent glassy thin films with high glass transition temperature above 100 °C.[9] Therefore, Bpy-OXD is highly amorphous materials. Amorphous molecular materials conventionally have bulky steric substituents and/or skeleton-twisting, but Bpy-OXDs do not have no such requests. We approach the origin of highly amorphous nature of this compound by means of computational methods.

Figure 4 shows the lowest and second lowest total energy geometries of Bpy-OXD. The lowest geometry looks like planar "S", and the second geometry shapes like helical "C". That is, atomic arrangements in space are quite different each other. On the other hand, the total energies for each geometries, however, are quite close, and the energy difference (ΔE) of 0.378 kcal/mol is smaller than the thermal energy of 0.5925 kcal/mol at room temperature (298.15K). Furthermore, the mutual alternation between the two geometries occurs only rotation around a single bond connecting the central phenyl ring and the adjacent oxadiazole ring. As shown in Fig. 4(c), the alternation in free space only requires 6 kcal/mol for activation because of no steric barrier and less π-conjugation between phenylene and oxadiazole based on weak conjugation in "–C=N–N=C–" bonds of oxadiazole. Since the estimated activation energy is within almost 10 times of the thermal energy, the alternation frequently occurs when the molecules are in free space. However, since the alternation needs a large excluded volume, the volume effect strongly restricts the alternation in solid states such as deposited films. We suppose at present that the highly amorphous nature of Bpy-OXDs probably results from a compositive reason of these effects.

In conclusion, the bipyridyl substituted oxadiazole (Bpy-OXD) that previously reported as an excellent ET layer material showed high electron mobility that reached above 10^{-3} cm^2/Vs. We believe the high mobility resulted from both the hybrid molecular structure of the two electron-accepting units and the planar molecular structure based on its no steric hindrance and no bulky substituent. The computational analysis demonstrated that the amorphous nature probably resulted from the polymorphic effect in isolate state and the volume effect in solid state.

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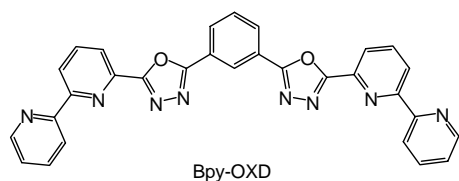
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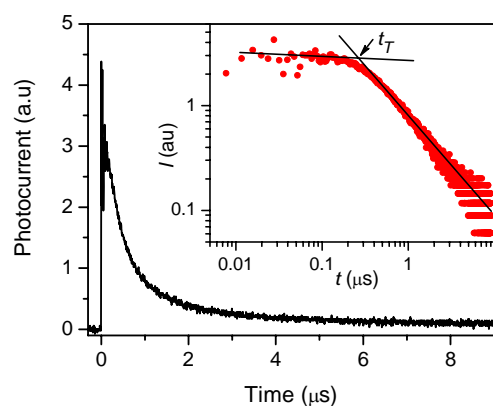Fig. 1. Chemical structure of Bpy-OXD.

Fig. 2. Electron transport TOF waveform of Bpy-OXD solid film at 1.15 MV/cm. The inset shows double logarithmic plot of the waveform.
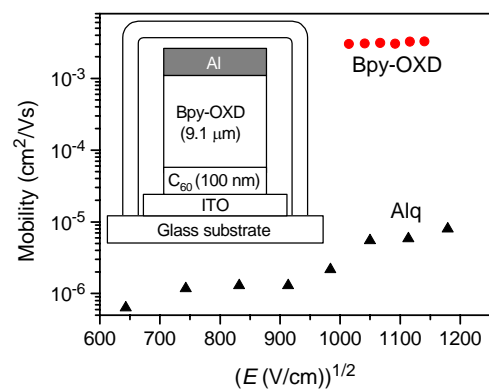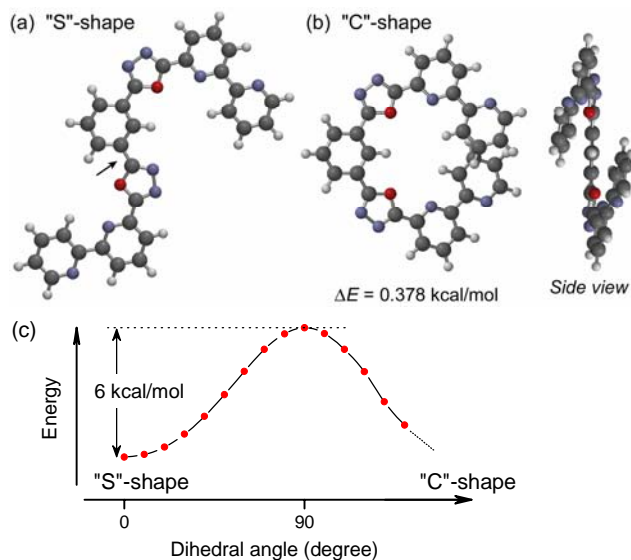

Fig. 3. Electric field dependence of electron mobility for Bpy-OXD. Inset: the structure of the test device. The device was encapsulated in pure N_2 gas with a freash descicant.

Fig. 4. The first (a) and second (b) optimized geometries of Bpy-OXD and the energy difference (ΔE) between the two geometries, which were obtained with the density functional theory (DFT) method of a commercial package (Wavefunction, Spartan 04W) with, respectively, B3LYP/6-31G(d) for geometrical optimizations and B3LYP/6-311+G(d, p) for energy calculations. (c): Energy profile of the alternation from "S"- to "C"-shapes, where the profile was obtained through geometry optimizations and energy calculations with rigid dihedral angles around the single bond indicated with the arrow in Fig. 4(a) by the same DFT procedures.