Efficient Electron Injection Characteristics of Triazine Derivatives for Transparent OLEDs (TOLEDs)

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We demonstrated that triazine (TRZ) derivatives possessing metal coordination sites in their structures showed excellent electron transport and injection characteristics in transparent organic light emitting diodes (TOLEDs). High luminescence efficiency with low driving voltage was observed with a TRZ/ITO cathode configuration (ITO: indium-tin-oxide), suggesting that the TRZ layer can efficiently accept electrons from the metal-oxide cathode layer, and inject electrons into an adjacent organic layer.

The exploration of novel electron transport materials is still a significant topic for various applications of organic light emitting diodes (OLEDs). In particular, efficient electron injection from a transparent indium–tin–oxide (ITO) cathode into an electron transport layer has been expected in transparent OLEDs (TOLEDs), which will lead to many unique OLED applications, such as top-emission OLEDs on a Si-substrate, flexible OLED displays,[1] and organic semiconductor laser diodes.[2] However, so far, very few materials have been utilized as an electron transport and injection material. The main ones that have the property are bathocuproine (BCP),[3] bathophenanthroline (BPhen),[4] tetra-2-pyridinylpyrazine (TPP),[5] and phthalocyanine derivatives. In this study, we demonstrate that triazine (TRZ) derivatives have excellent electron injection and transport characteristics in TOLED structures. In particular, we focused on the molecular design of TRZ derivatives to achieve efficient electron injection at the interface between the TRZ layer and the ITO cathode layer by changing the substituent groups of the TRZ derivatives.

We prepared TOLED device structures of an ITO anode/ 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl(α-NPD)/tris-(8-hydroxyquinoline)aluminum(Alq$_3$)/electron injection layer-(EIL)/ITO cathode. The top ITO cathode layer was fabricated by conventional magnetron sputtering under a pressure of 1×10^{-1} Pa with Ar (11.4 standard cc per minute; sccm) and O$_2$ (0.6 sccm) gas flow and sputtering power of 20 W. We set the substrate and sputtering target at a fixed angle ($40°$) and distance (50 mm) to minimize sputtering damage. In a separate experiment, we optimized these parameters.[6] TRZ derivatives were synthesized according to a previous report[7] and purified by a train sublimation before device fabrication. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels were determined with an AC-1 (Riken Keiki Co.) and a conventional UV–vis absorption spectrometer, respectively. Current density (J), voltage (V) and luminance (L) characteristics were measured using an HP4145 semiconductor parameter analyzer with the quantum efficiency directly obtained by placing and centering the OLEDs onto the surface of
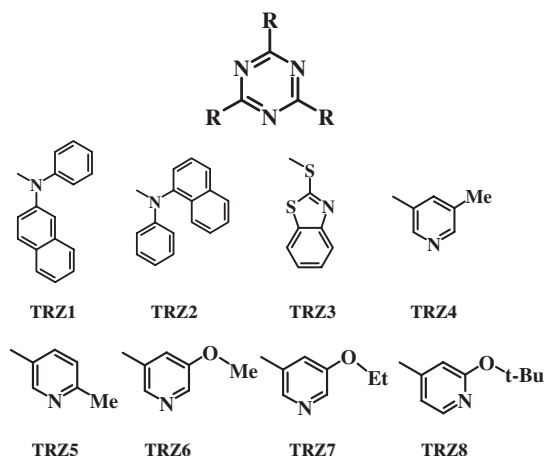

Figure 1. Molecular structures of triazine derivatives.

a large diameter calibrated Si-photodiode. Figure 1 shows the molecular structures of TRZ derivatives used as an EIL in TOLEDs. These TRZ derivatives were composed of a triazine core with various substituents.

Figure 2 shows the J–V characteristics of TOLED with TRZ4 ($\diamond$) and BCP ($\bigcirc$) as the EIL. For reference, TOLED characteristics without the EIL (control device) are also shown ($\blacksquare$). In the device with TRZ4 as the EIL, the highest current density
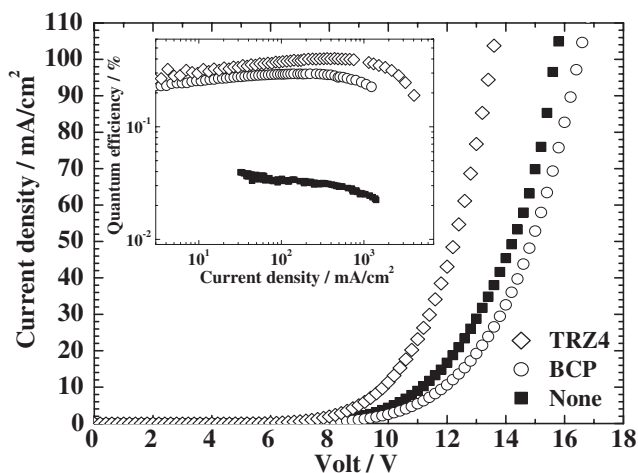

Figure 2. Current density versus voltage characteristics of ITO (110 nm)/α-NPD (50 nm)/Alq$_3$ (50 nm)/electron injection layer (EIL: 10 nm)/ITO (100 nm) devices: EIL=TRZ4 ($\diamond$), BCP ($\bigcirc$) and None ($\blacksquare$). (Inset) External EL quantum efficiency versus current density characteristics of these devices.

Table 1. Current density at an applied voltage of 10 V and the maximum η_{ext} in TOLEDs with TRZ derivatives as the EIL, the coordination site number, and HOMO/LUMO levels of the TRZ deposited layers

	J (mA/cm^2) at 10 V	η_{ext} /%	Coordination Number	HOMO/LUMO /eV
TRZ1	0.37	0.14	3	5.8/2.3
TRZ2	0.94	0.02	3	5.8/2.2
TRZ3	4.7	0.07	3	5.5/1.9
TRZ4	11.4	0.40	6	5.5/1.9
TRZ5	7.8	0.35	6	5.4/1.8
TRZ6	4.5	0.34	6	5.5/1.7
TRZ7	3.3	0.24	6	5.5/2.1
TRZ8	9.6	0.36	6	5.5/2.1
BCP	2.5	0.40	2 (chelation)	6.7/3.0
None (Alq$_3$)	4.3	0.04	0	5.8/3.2

of 100 mA/cm^2 was obtained at the applied voltage of 13.5 V, indicating efficient electron injection from an ITO cathode into the TRZ4 layer. On the other hand, in the other devices having BCP as the EIL or having no EIL, rather higher driving voltages were required to obtain 100 mA/cm^2. The external electroluminescence (EL) quantum efficiency (η_{ext}) vs J characteristics is shown in the inset of Figure 2. Compared with the device without an EIL, the devices having TRZ4 and BCP as the EIL demonstrated high η_{ext} values, and the highest η_{ext} of approximately 0.4% was obtained with TRZ4. Thus, we have demonstrated that the TRZ4 layer can efficiently accept electrons from an ITO cathode and transport and inject them into the adjacent Alq$_3$ layer.

Table 1 summarizes J at an applied voltage of 10 V, the maximum η_{ext} in the TOLEDs with the TRZ derivatives as the EIL, the coordination site number of TRZ derivatives, and the HOMO/LUMO levels of the TRZ deposited layers. Here, the triazine core has three coordination sites and the substituent pyridine ring has one coordination site, although we can assume that the arylamine structures have virtually no coordination effects due to steric hindrance. We recognize that the TRZ derivatives (TRZ4-8) having six coordination sites resulted in higher η_{ext}, while TRZ1, 2, and 3 having three coordination sites resulted in low η_{ext}. In particular, TRZ2 has a large steric hindrance due to the presence of the bulky α-naphthyl group, which presumably makes it difficult to coordinate with sputtered InO$_x$ or SnO$_x$ clusters, although TRZ4 has a planar molecular structure, which is advantageous for coordination between TRZ4 and the sputtered atoms. Here, we also mention the substitution effect of TRZ4-8. Since the benzothiazole group in TRZ3 has large steric hindrance, it presumably obscures coordination effect of the N atoms in the triazine cores. Further, since we observed weak effect in an increase of η_{ext} in TRZ3, the benzothiazole group itself has weak coordination effect. In addition, we can also assume that O atom in the ether of TRZ6-8 has no coordination effect, since there is no significant difference of η_{ext} in the devices with TRZ4-8.

In order to understand the efficient electron injection mechanism from an ITO cathode, we measured how the maximum η_{ext} depended on TRZ4 thickness. We compared two cathode configurations: ITO (110 nm)/α-NPD (50 nm)/Alq$_3$ (50 nm)/ TRZ4 (X nm)/cathode with cathode = MgAg (100 nm)/Ag (10 nm) and ITO (100 nm). Although the devices with the
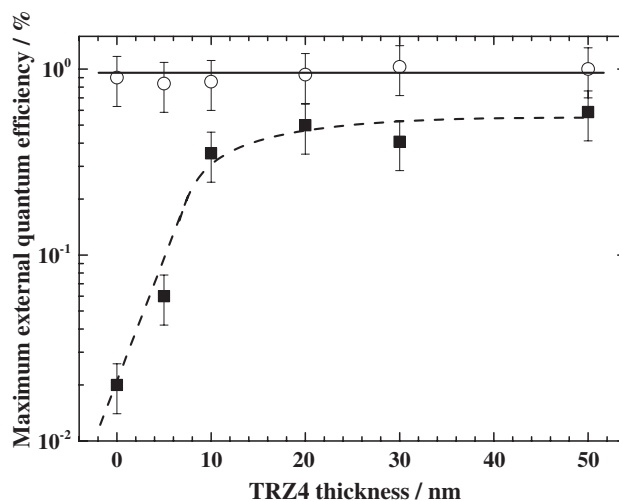
Figure 3. Dependence of maximum external EL quantum efficiency on thickness of the TRZ4 layer in two cathode structures: ITO (110 nm)/α-NPD (50 nm)/Alq$_3$ (50 nm)/TRZ4 (X nm)/cathode with cathode = MgAg (100 nm)/Ag (10 nm) [○] and ITO (100 nm) [■].

MgAg/Ag cathode showed maximum η_{ext} of 1.0%, which was independent of the TRZ thickness, the device with an ITO cathode showed the characteristic thickness dependence (Figure 3). While high quantum efficiency of $\eta_{ext} \approx 0.4\%$ was obtained with TRZ4 thicker than 10 nm, the maximum η_{ext} rapidly decreased for thinner TRZ4 layers. This suggests that the sputtered metal-oxides penetrate into the TRZ4 layer to a depth of about 10 nm. When the TRZ4 thickness was less than 10 nm, the TRZ4 deposited films have an island structure and the metal-oxides migrated into the TRZ4 layer and directly attached to the Alq$_3$ layer. In this case, the electron injection from ITO into the Alq$_3$ layers was inefficient, perhaps because of unknown damage or interaction between Alq$_3$ and the sputtered metal-oxides during the ITO formation process. On the other hand, when the TRZ4 layer was thicker than about 10 nm, efficient electron injection was achieved by the TRZ4/ITO interface based on the metal coordination effect. The dependence of these characteristics on the thickness of the TRZ4 layer is consistent with previous reports using a thin metal layer as a protective layer.[3,8]

In summary, we demonstrated efficient electron injection from an ITO cathode into TRZ layers. TRZ derivatives having a large coordination number showed rather high η_{ext}, demonstrating that the TRZ layer functions as the EIL and as a protective layer for ITO deposition.

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